

# The 2018 EXPORTS Pacific Experiment

## Calibration of the SUNA Nitrate Sensor on Lagrangian Float #92

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### Summary

The Seabird SUNA Nitrate sensor on the EXPORTS Lagrangian float (#92) was calibrated using bottle samples from the *R/V Revelle* and *CCGS Tully* spanning 16 August 2018 to 22 September 2018. Nitrate values computed in real time by the SUNA were about 5  $\mu\text{mol/L}$  high relative to the bottles. The spectral data were reprocessed using SUNAcomm 3.0 and Seabird UCI 2.0.2\_828 software and in house MBARI software; these differed by less than 0.1  $\mu\text{mol/L}$  below 10m. Comparison with the bottles was done in the mixed layer and at potential density values from 24.7 to 26.7  $\text{kg m}^{-3}$ . The EXPORTS region was sufficiently homogeneous that calibration results are insensitive to how intercomparison casts were selected; time differences from 7 to 12 hours and distances from 3-30 km yielded similar results. The reprocessed nitrate values averaged about 0.8  $\mu\text{mol/L}$  low relative to the bottles at the start of the interval and differed by less than 0.2  $\mu\text{mol/L}$  by the end. This time varying bias is removed with a calibration offset to yield the final calibrated nitrate values. The calibration points deviate from this by about 0.2  $\mu\text{mol/L}$  rms. Additional bottle samples taken on 2 December 2018, at the end of the deployment, did not yield usable results. Thus, nitrate data taken after 22 September 2018 is not calibrated. Additional drifts of several  $\mu\text{mol/L}$  are possible. This report applies to EXPORTS Lagrangian Float data release

***EXPORTS-EXPORTSNP\_suna\_LagrangianFloat\_20180812\_R2.sb.***

### 1. Sensors & Mission

Float 92 (Fig 1) was the only Lagrangian float deployed in EXPORTS 2018. It carried SBE-41-CT sensors on the top and bottom endcaps with the entrances to the sensors separated vertically by 1.7 m. A v1 SUNA UV nitrate sensor (SN 096) was mounted near the bottom of the float (see Figure 1). Exhaust from the bottom CTD was pumped into the SUNA sampling chamber using a SUNA flow-through cell. Float 92 was deployed on 14-Aug-2018 07:15Z from the *R/V Sally Ride*, sampled for 109.3 days with the last data taken on 01-Dec-2018 14:34 Z. The float was recovered shortly thereafter by *R/V Sikuliaq*. The SUNA sampled 8834 data points, with an average separation of ~1000 seconds. The float also successfully measured temperature, salinity, pressure, oxygen,

optical backscatter and chlorophyll fluorescence. The accuracy of these sensors will be described in other data reports.

Calibration casts were made from the *R/V Revelle* and *R/V Sally Ride* during the main experimental period, from the *CCGS Tully*, in late September and from the *R/V Sikuliaq* at recovery. Only data from the *R/V Revelle* and *CCGS Tully* were of sufficient quality to be used for calibration.

The float executed a simple mission (Fig. 2) alternating between daily profiles to 200m and a Lagrangian drift at approximately 100 m. More precisely, during the drift the float targeted the  $25.85 \text{ kg m}^{-3}$  isopycnal maintaining this isopycnal between the top and bottom CTDs as it moved vertically  $\pm 10\text{m}$  due to internal waves and tides and mesoscale eddies (Fig. 3). Profiles occurred once per day, timed to approximating 0130Z during the cruises so as to facilitate calibration casts, and to approximately 1300Z thereafter, so as to facilitate nighttime air calibrations of the oxygen probe.



Figure 1. Sensors at bottom of EXPORTS float 92.

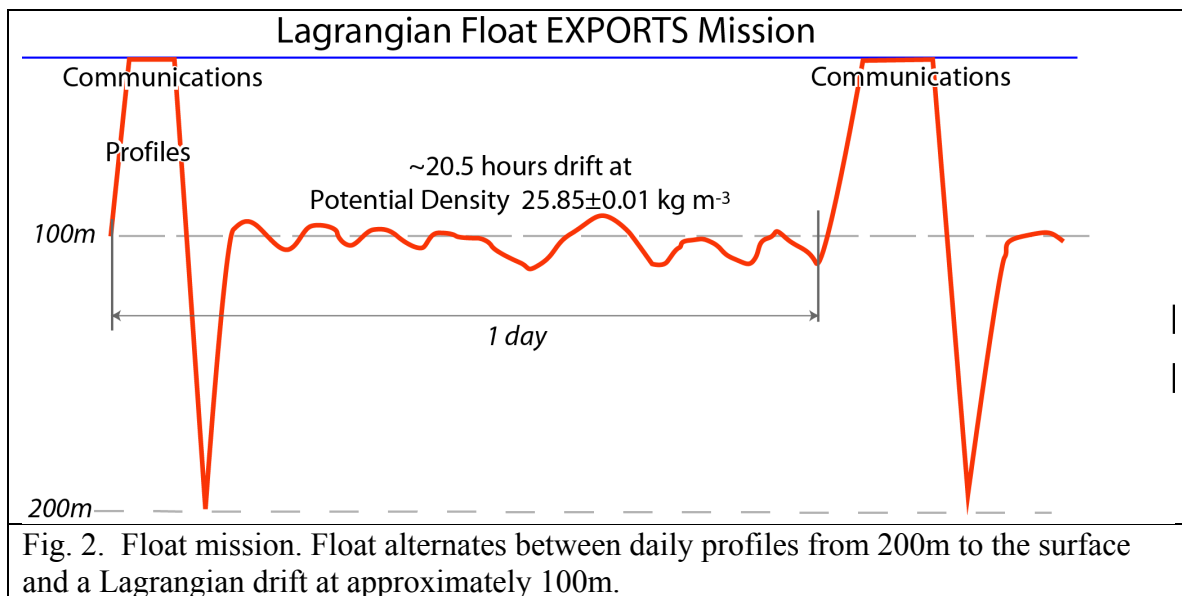


Fig. 2. Float mission. Float alternates between daily profiles from 200m to the surface and a Lagrangian drift at approximately 100m.

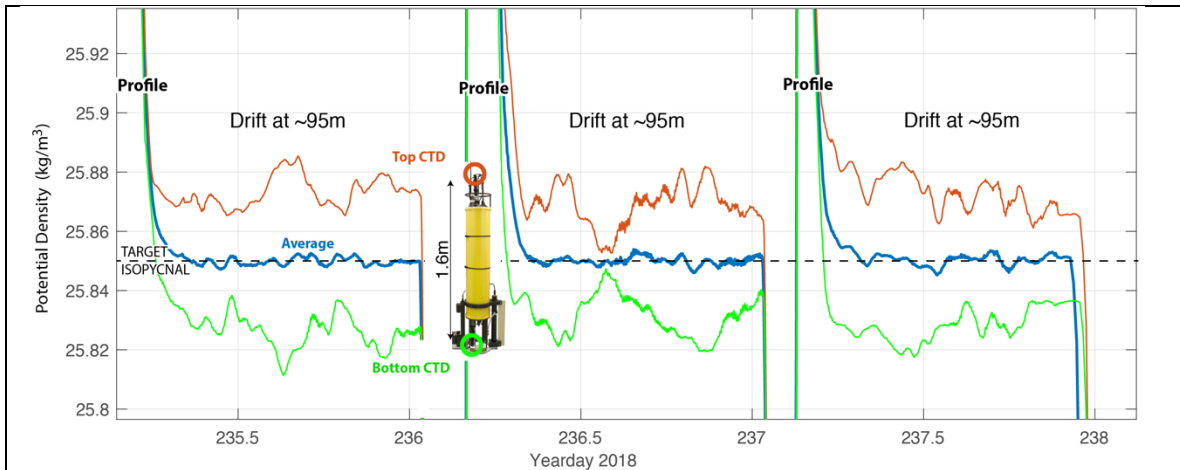


Fig. 3. Example of isopycnal drift. Float straddles target isopycnal with an accuracy of about 0.1 m.

The CTD sensors on the float were sampled every 100s during the drift and 15-75s during profiles depending on other activities. Other sensors were sampled less frequently, mostly to save energy. The SUNA, due to its high power consumption, was sampled every 17<sup>th</sup> time during drifts (intervals of 128s, 256s and 384s), and every 5<sup>th</sup> time during profiles (intervals of 1664s and 1792s).

## 2. SUNA Processing

On each sample, the SUNA measures the spectrum of light absorption in the ultraviolet from 190–370 nm. These spectra are fit with absorption curves for bromide, the relevant component of salinity, nitrate and organic matter. The results are somewhat sensitive to the wavenumber range used for fitting. Analysis here used 216.5-240 nm. The SUNA does not measure salinity, so the realtime data stream estimates salinity from the absorption spectrum. Postprocessing (Sakamoto et al. 2009) uses salinity and temperature from a CTD to subtract the salinity contribution, and corrects the measured absorption spectra for temperature, resulting in more accurate nitrate estimates with less noise.

The dataflow for the SUNA processing is shown in Appendix B. The Lagrangian float downloaded and stored the raw spectral files from the SUNA in the *suna\*.dat* files along with CTD and engineering data files as L0 data. These are processed to L1 without calibration *Env.mat* and *SX.mat*. The figure outlines the dataflow to create L2 data by reprocess these spectra and comparing with bottle data.

The float SUNA data was first post-processed using SUNAcomm 3.09. This program was released by Seabird in 2012 and is no longer supported. Calibration coefficients from a pre-cruise calibration (23-Feb-2018) were used. A post-cruise calibration (April 2019) reported a ‘scratched window’. This calibration was therefore not used. Substantial modifications in the file headers were necessary to make the program work and the input data had to be split into 3 separate files to keep the program from crashing. The post-

processed values of nitrate were about 5  $\mu\text{mol/L}$  lower than the realtime values and showed different variations with depth and time. These is a large change and it was unclear whether the reprocessing program had been operating properly.

The above post-processing was checked at MBARI using SeaBird's [UCI 2.02\\_828](#) software and a variant of MBARI's own processing software which included a small correction for the pressure coefficient of bromide (Sakamoto et al. 2017). The differences between the values of nitrate computed by these and by SUNAcomm 3.09 are less than 0.2  $\mu\text{mol/L}$  and larger at depth. These differences are smaller than the accuracy of the instrument. The SUNAcomm reprocessed data was thus used.

### 3. Calibration with Bottle data

SUNA data was calibrated using bottle data from *R/V Revelle* and *CCGS Tully*. The CTD bottle casts sampled at discrete depths over a short time interval while the float only profiled once per day. Since *Revelle* was not tasked with taking calibration cast there are very few close space/time matchups; no *Revelle* casts were within 1 hour and 1 km of a float profile. However, unlike in more dynamic regions (Alkire and D'Asaro 2010), the ocean is quite homogeneous in this region, so much larger space and time differences still led to a good calibration.

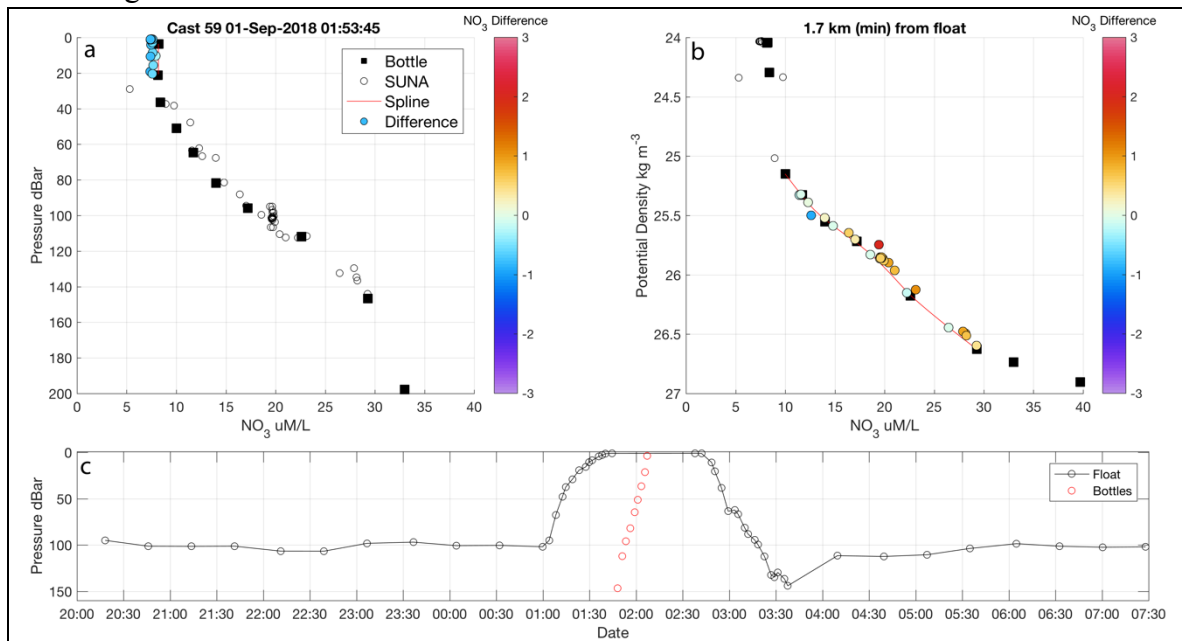


Figure 4. Example comparison between nitrate values from CTD bottle cast and Lagrangian float SUNA. Cast number, Cast time and minimum distance from float are noted in panel titles. Cast numbers for IOS are event+100. a) Profile from bottles (black squares) and from SUNA as a function of pressure. Bottle data shallower than 26 dbar is averaged to form a mixed layer value (red line). SUNA data shallower than 26 dbar is colored by the difference from this value. b) . a) Profile from bottles (black squares) and from SUNA as a function of potential density. Bottle data between 24.7 and 26.7  $\text{kg m}^{-3}$  is fit with a smoothing spline (red line). SUNA data in this same density range is colored by the difference from this value. c) Depth of float (black) and bottles (red) for data used in the figure.



Figure 4 shows how these bottles and SUNA were compared. Mixed layer comparisons (Fig. 4a) were made with data shallower than 26 dbar. Bottle data was averaged to form a mixed layer value and SUNA data compared with this average. Pycnocline comparisons (Fig. 4b) were made with data in a potential density range of  $24.7\text{--}26.7\text{ kg m}^{-3}$ . SUNA data was compared to values from a smoothing spline through bottle samples in this range. Plots for all casts used in the SUNA calibration are shown in Appendix B. Note that in the mixed layer the SUNA values fall slightly below the bottle values so that the dots are colored blue, while in the pycnocline they are closer to the bottle values so that the dots are both red and blue. This difference occurs throughout the dataset. Accordingly, the mixed layer and pycnocline are analyzed separately.

Figure 5 summarizes the difference between SUNA and bottle values. The small dots in show the deviation of each SUNA measurements from the interpolated bottle data, either the mixed layer mean value (blue dots) or the pycnocline splined values (red dots). The mean of these values is shown by the larger dots, cyan for the mixed layer and magenta for the pycnocline, and their standard deviation is shown by the vertical lines, cyan and magenta for the mixed layer and pycnocline respectively. Overall, the SUNA data are within about  $1\text{ }\mu\text{mol/L}$  of the bottle data, close to the rms accuracy achieved by Sakamoto (2009) of  $0.65\text{ }\mu\text{mol/L}$ .

The two panels of Figure 5 show two data from two different sets of comparison profiles. Fig. 5a used a very relaxed criterion to selection the CTD bottle casts, having a minimum distance of 30 km from the closest approach of the float within 12 hours of the cast; 29 calibration casts are selected. Fig. 5b used a much tighter criterion, 4 km within 7.2 hours; 8 calibration casts are selected. Despite the large differences in the selection criteria, curves fit through the data points (dashed lines) yield results that differ only by a few times  $0.1\text{ }\mu\text{mol/L}$ , well below the accuracy of the instrument. Thus, the distribution of nitrate in this region is sufficiently homogeneous that casts separated by many 10's of km's have the same concentrations within the accuracy of the SUNA. The deviation of the calibration points from the dashed black curve is about  $0.5\text{ }\mu\text{mol/L}$ , comparable to Sakamoto et al. (2009)'s value of  $0.65\text{ }\mu\text{mol/L}$ .

Figure 5 separately calibrates mixed layer points (blue) and pycnocline points (red). The SUNA measures about  $0.8\text{ }\mu\text{mol/L}$  lower in the pycnocline, relative to the bottles, than in the mixed layer. The reason for this is unknown.

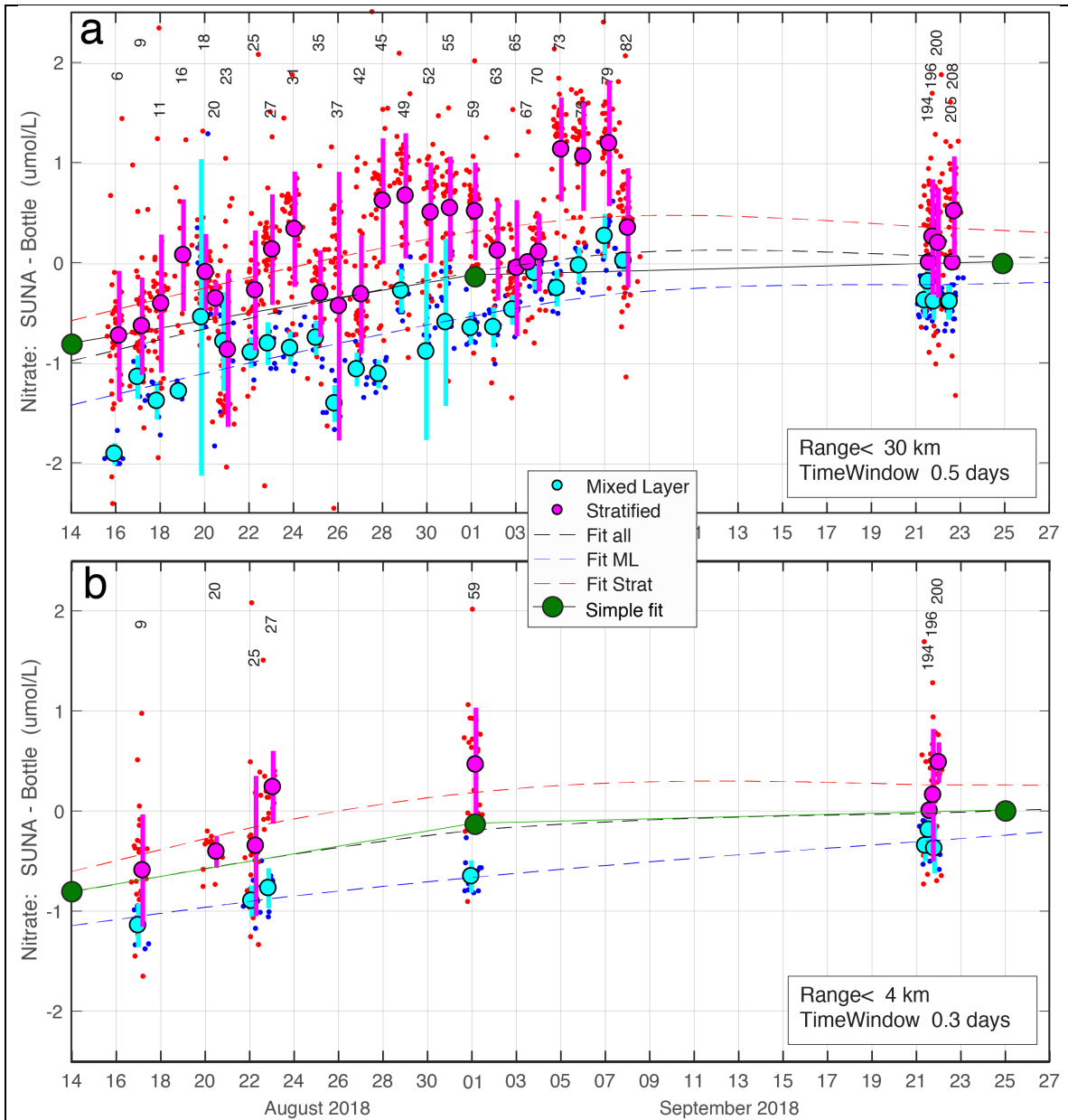


Figure 5. Deviation of SUNA from bottles (small dots) for a) loose selection criteria and b) strict selection criteria. Small numbers identify a unique cast number and reference the plots in Appendix C. For each cast, large circles mark average; vertical line shows  $\pm 1$  standard deviation. Bottles from the mixed layer are cyan/blue. Points from pycnocline are red/magenta. Dashed lines are smoothing spline fits as a function of time for all bottles (black), mixed layer bottles (blue) and pycnocline bottles (red). Large green dots and green line show final offsets applied to the data.

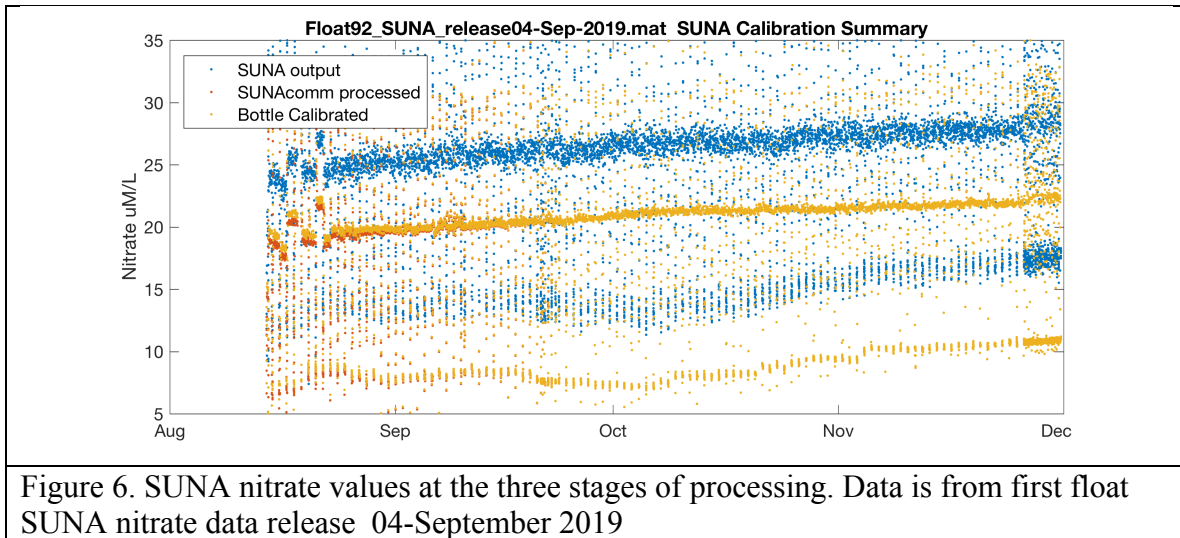


Figure 6. SUNA nitrate values at the three stages of processing. Data is from first float SUNA nitrate data release 04-September 2019

## 4. SUNA calibration and drift

A final calibration for the SUNA is shown by the green dots in Figure 5 which lie very close to the black dashed line fitting all of the calibration points in both panels. The released SUNA nitrate values will be the SUNAcmm values with the linear interpolation of the green dots subtracted.

Float data continued for 71 days past the last calibration cast through the float recovery on December 1, 2018. Calibration casts taken at recovery did not provide useful nitrate data. Given the data record for the first 40 days, drifts of several  $\mu\text{mol/L}$  are likely. The SUNA values are thus uncalibrated to this accuracy during this period. The released SUNA nitrate values will be the SUNAcmm values.

Figure 6 summarizes the calibration procedure. The realtime SUNA data is about 5  $\mu\text{mol/L}$  high. Reprocessing with the Sakamoto algorithm using SUNAcmm 3.09 removes this bias. Adjusting this to the bottle makes a small additional change.

## 5. Summary

The realtime nitrate data from float 92 SUNA 0096 is about 5  $\mu\text{mol/L}$  high. Reprocessing using the Sakamoto et al. (2009) algorithm removes most of this bias. Appendix B lists a function that remove the small remaining bias relative to bottle samples from the *R/V Revelle* and *CCGS Tully* cruises. SUNA data after 22 September is not calibrated against bottles.

The float SUNA data release is  
***EXPORTS-EXPORTSNP\_suna\_LagrangianFloat\_20180812\_R2.sb.***

A Matlab version of this data is also available from the first author.

Date & time	From GPS. Accuracy of 1 s
lat,lon	Position interpolated from GPS surfacings. Accuracy at each surfacing 10m
pressure	Pressure at bottom CTD, dbar
sal,wt	salinity and temperature at bottom CTD, psu and C
NO3_1id	Realtime nitrate $\mu\text{mol/L}$
NO3_2id	nitrate after processing with SUNAcomm 3.09. $\mu\text{mol/L}$
NO3	Final nitrate after correcting with bottles. $\mu\text{mol/L}$

## References

D'Asaro, E. (2011) Nitrate plus raw spectral profiles from a Satlantic Nitrate Sensor on Biofloat 48 in the subpolar North Atlantic and Iceland Basin in 2008 (NAB 2008 project). Biological and Chemical Oceanography Data Management Office (BCO-DMO). Dataset version 2011-03-15. <http://lod.bco-dmo.org/id/dataset/3442>

Sakamoto, C.M., Johnson, K.S. and Coletti, L.J., 2009. Improved algorithm for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer. *Limnology and Oceanography: Methods*, 7(1), pp.132-143.

Sakamoto, C.M., Johnson, K.S., Coletti, L.J. and Jannasch, H.W., 2017. Pressure correction for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer. *Limnology and Oceanography: Methods*, 15(10), pp.897-902

## APPENDIX A

```
function [suna] = SUNACommCal(suna_in)
% [suna] = SUNACommCal(suna_in)
% Calibrates 2018 EXPORTS Pacific data from float 92 SUNA (s/n 0096)
% to water samples on the R/V Revelle and CCGS Tully cruises.
% Data taken after September 22, 2018 is not calibrated further and
% may contain drifts of several umol/L to the end of data
%
% The input data structure suna contains at least
%   suna_in.mtime - Matlab time
%   suna_in.nitrate_SUNAComm- nitrate computed by SUNAcomm 3.0 from spectra
%   Other variables are also allowed
%
% The output data structure adds the variables
%   suna.times - calibration point times
%   suna.offsets- offsets
%   suna.nitrate_cal - nitrate calibrated to bottles
%
% Eric D'Asaro   September 3, 2019

suna=suna_in;
suna.CalibratedNitrate=suna_in.SUNACommNitrate; % output nitrate- first set to
input

% CALIBRATION POINTS FOR 2018 EXPORTS
suna.offsets = -[ -0.8018  -0.1225 0];
qtimesS={ '14-Aug-2018 02:04:23'  '01-Sep-2018 01:19:09'  '25-Sep-2018
00:18:50'};

suna.times=datetime(qtimesS);

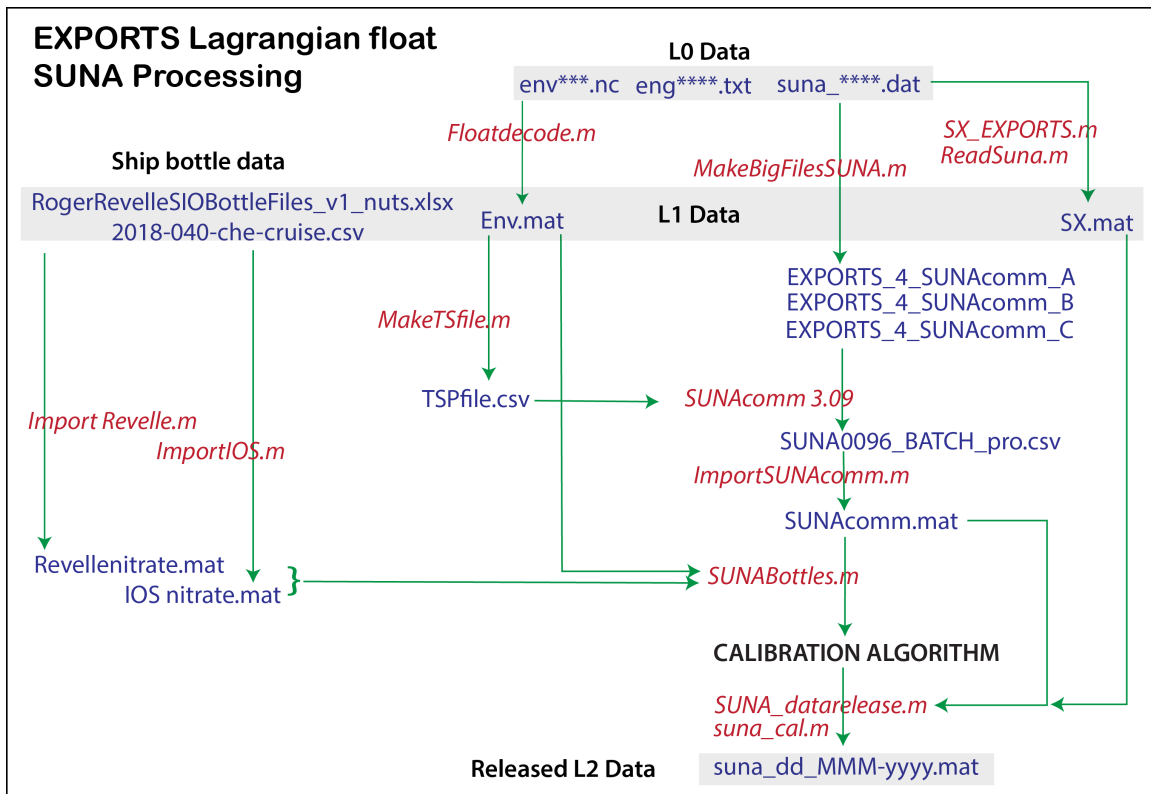
% change output nitrate where we have calibration points
g=find(suna.mtime<suna.times(3) & suna.mtime>suna.times(1) );
suna.CalibratedNitrate(g)=suna_in.SUNACommNitrate(g)+interp1(suna.times,suna.of
fsets,suna.mtime(g) );

suna.meta.CalibratedNitrate='SUNAComm nitrate calibrated to EXPORTS 2018
bottles';
suna.meta.times='Times of calibration points. Data outside this range equals
SUNAComm values';
suna.meta.offsets='Offset at each calibration point. Add this to SUNAcomm value
to get calibrated value.';

end
```

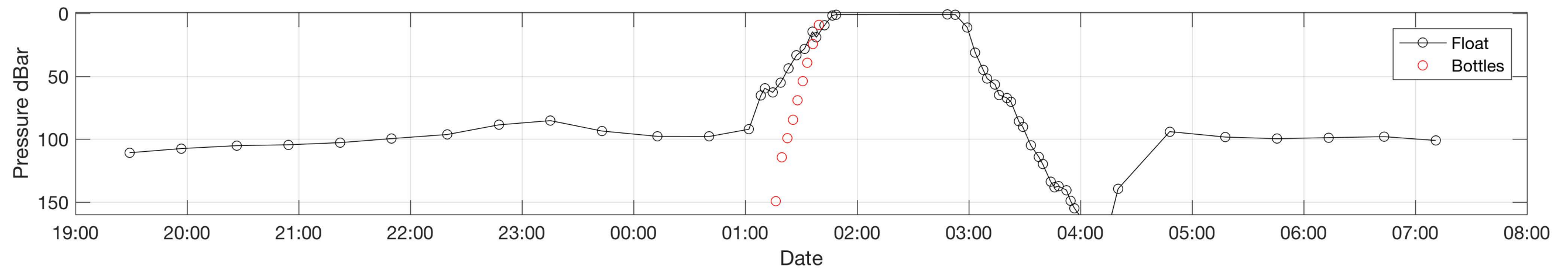
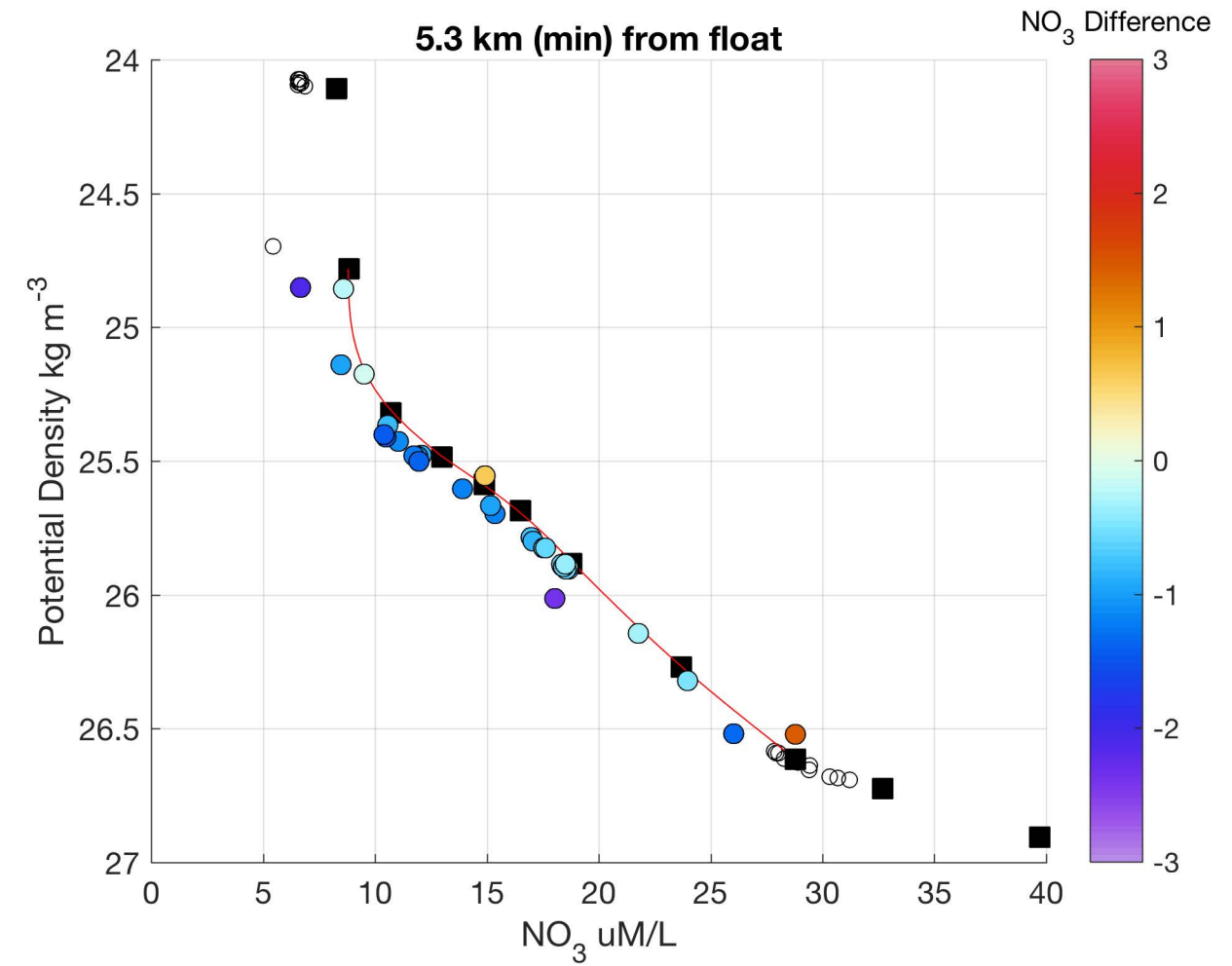
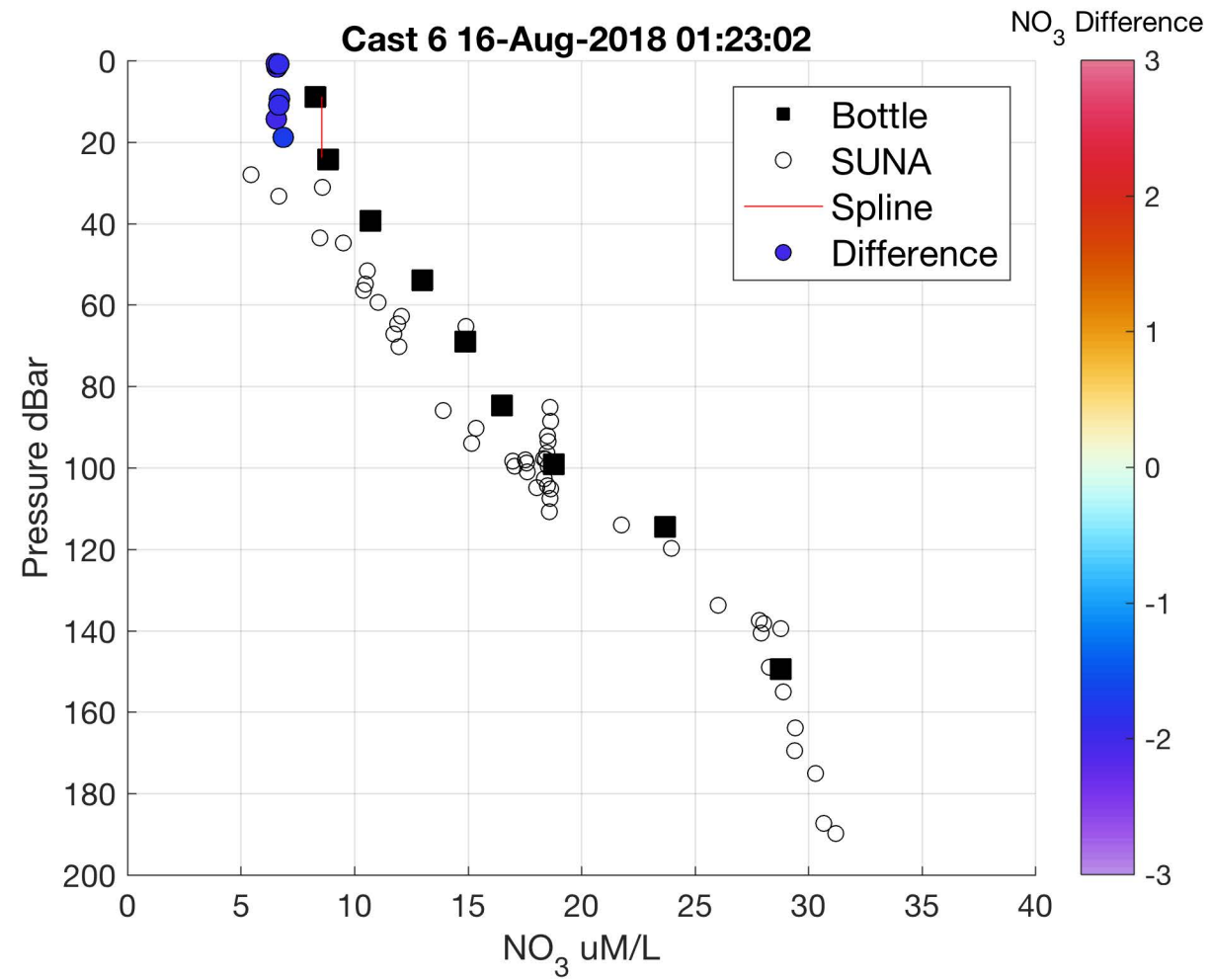
## APPENDIX B

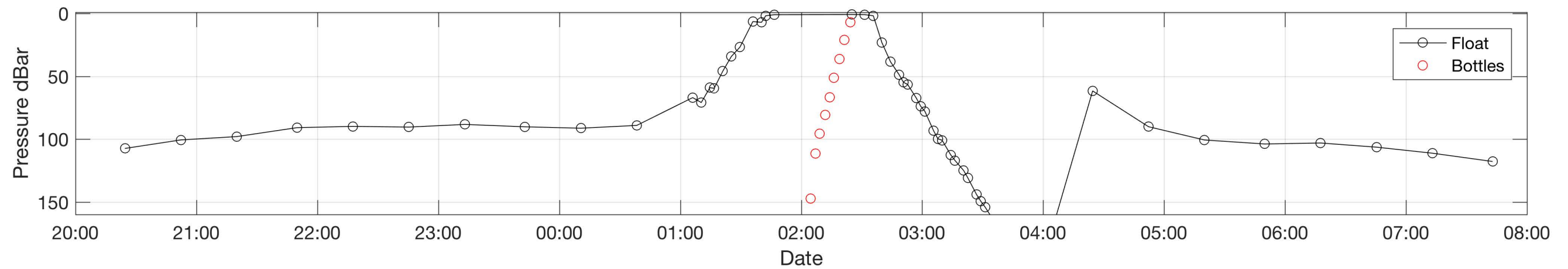
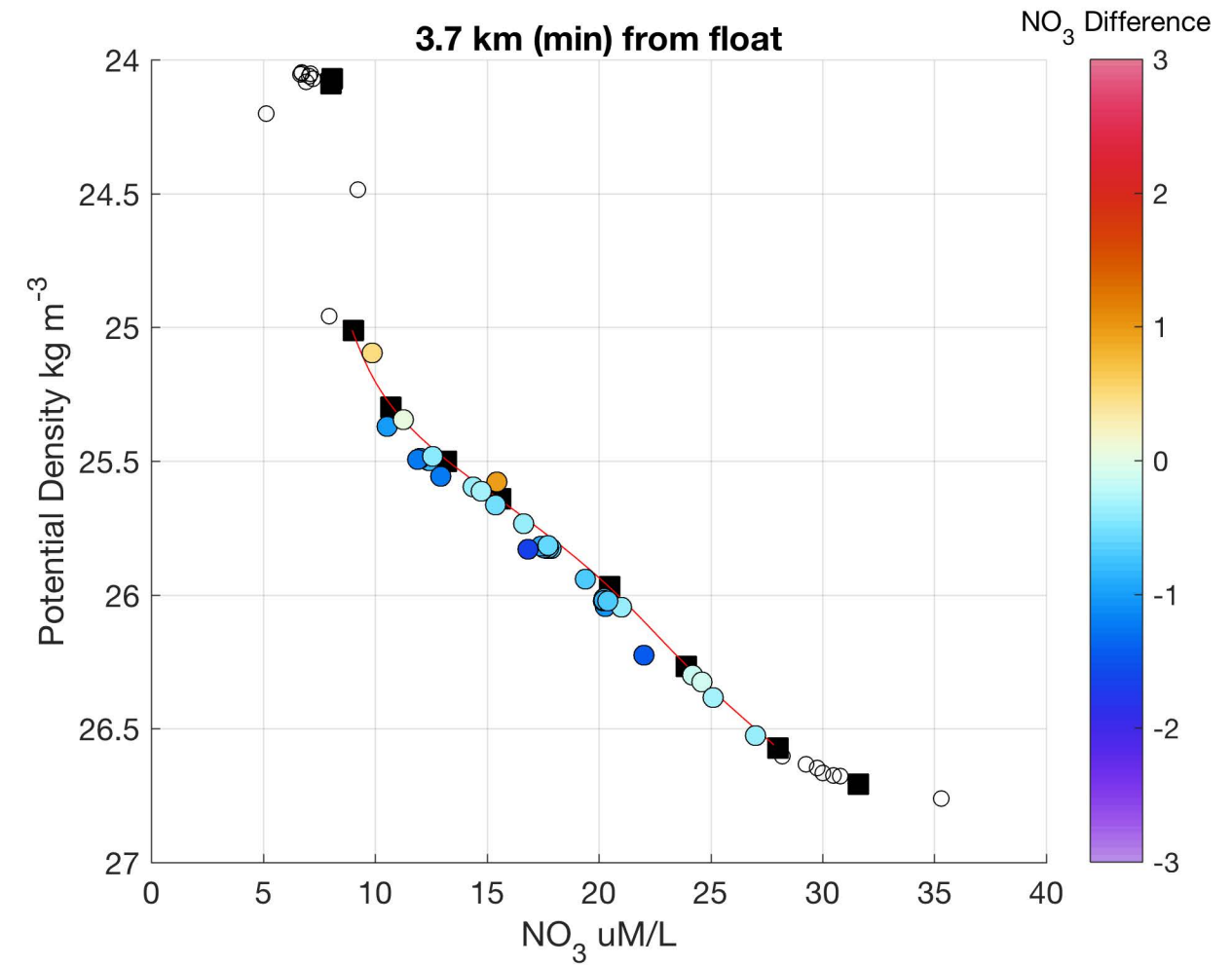
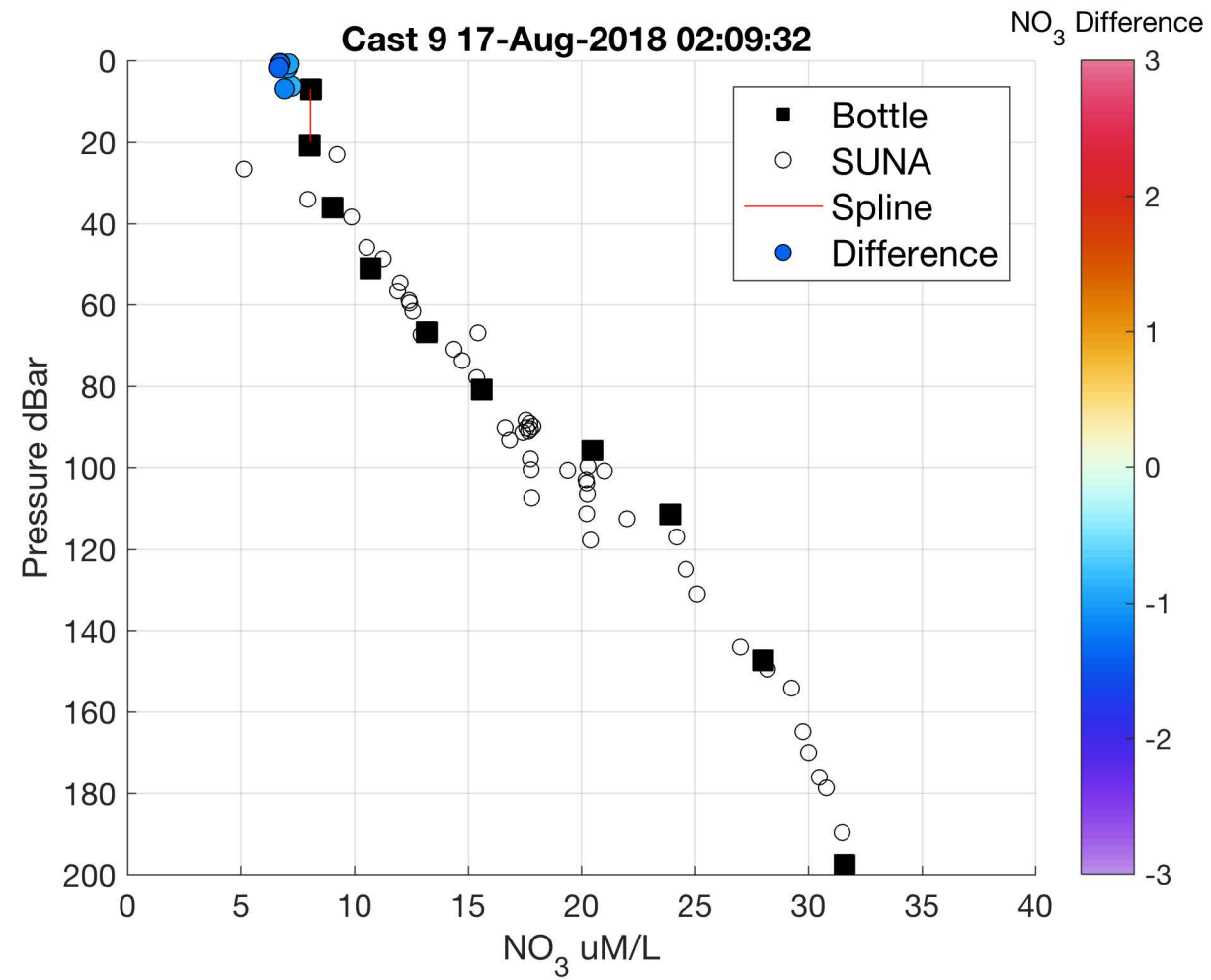
Data flow for Lagrangian float data processing. Files are blue. Programs are red. Data flows along green arrows between files.

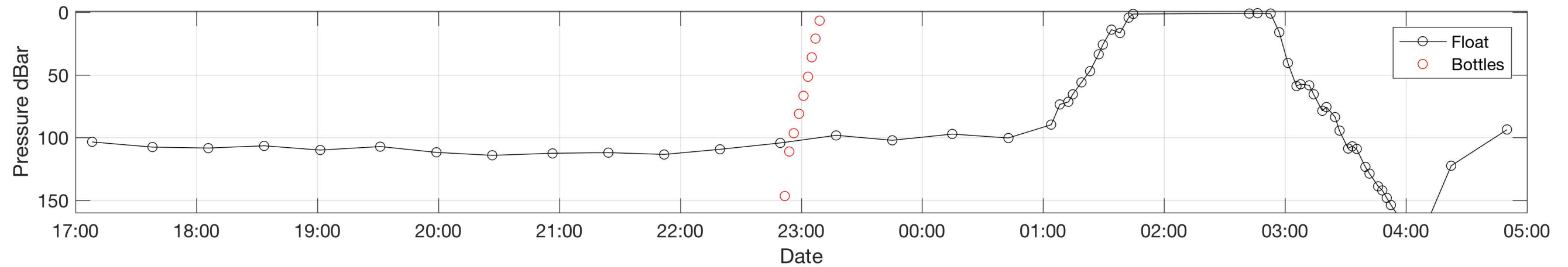
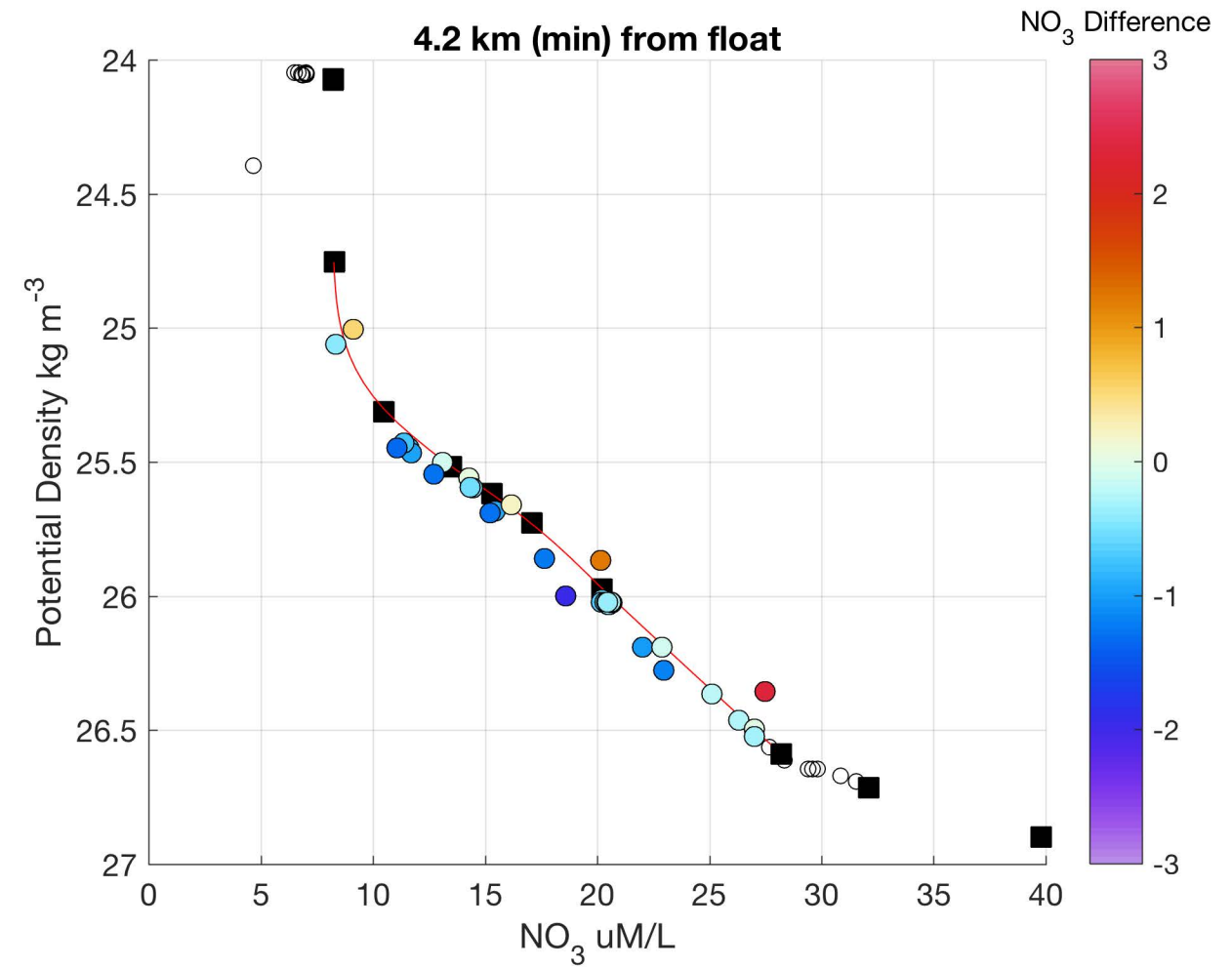
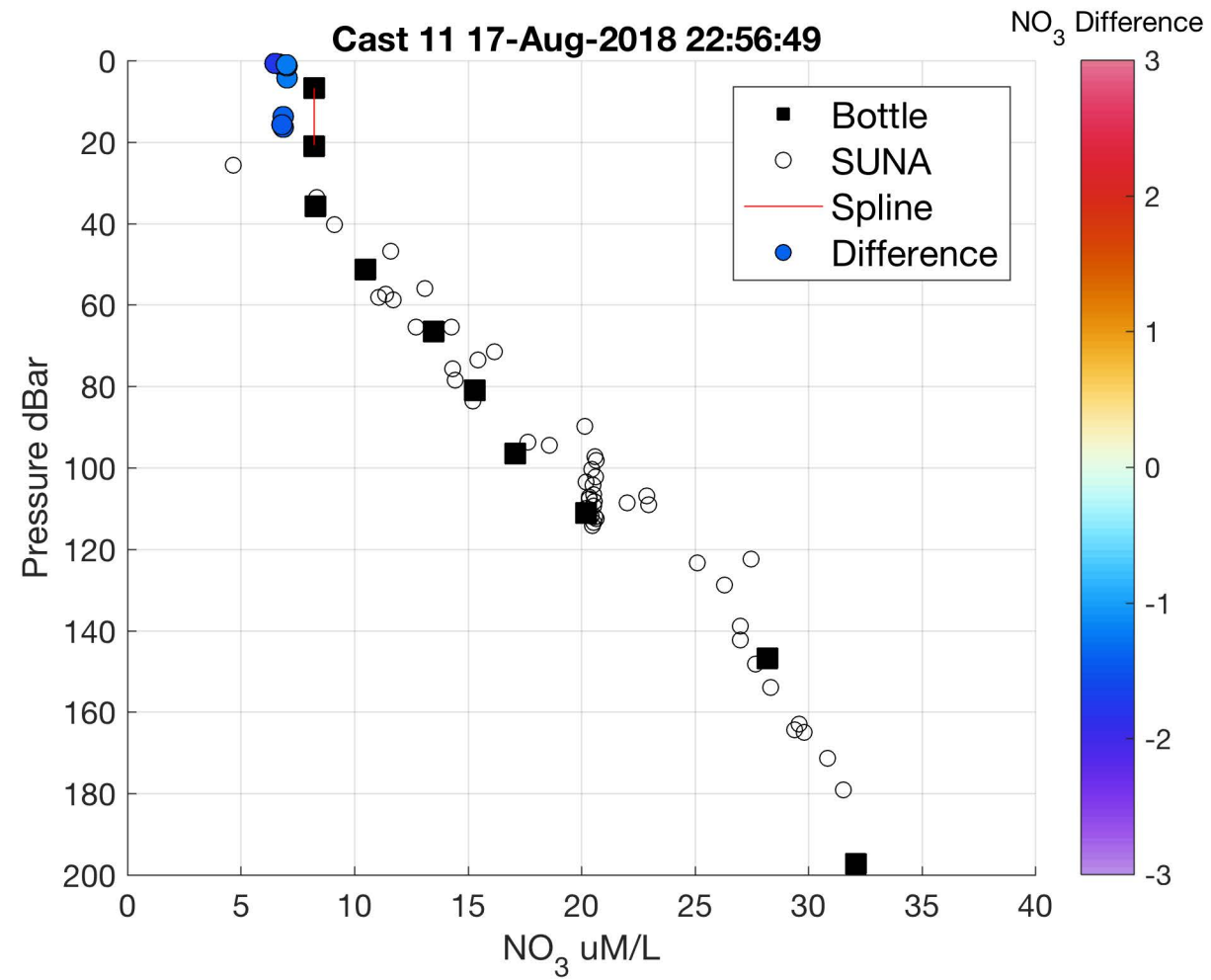


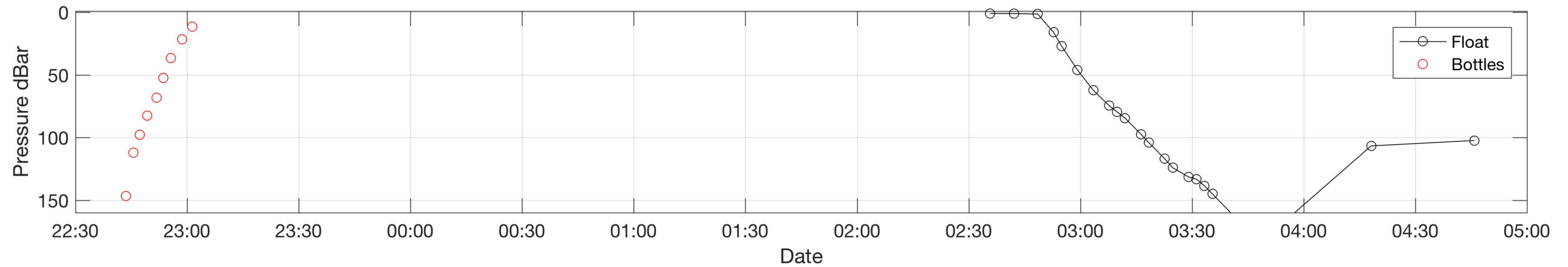
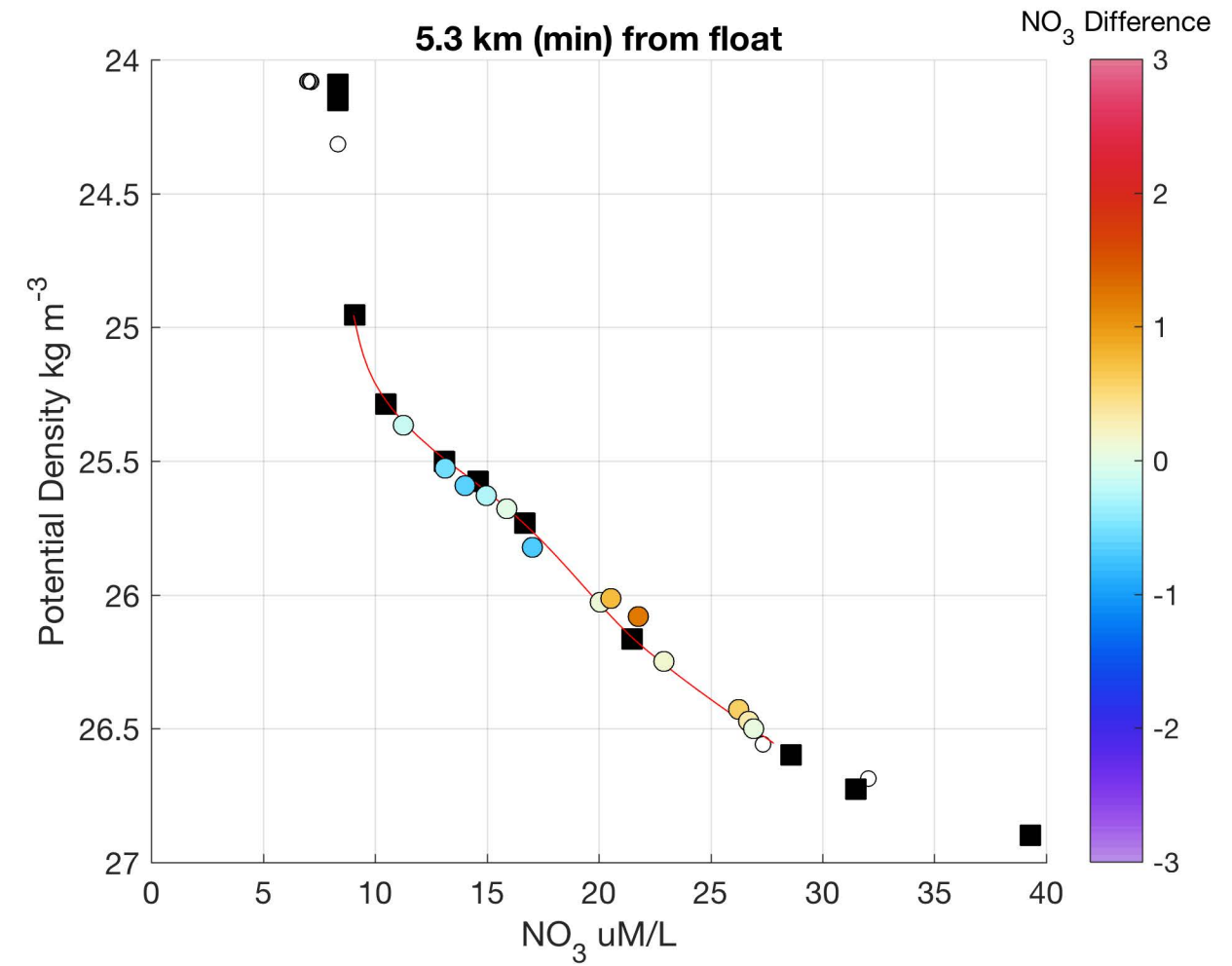
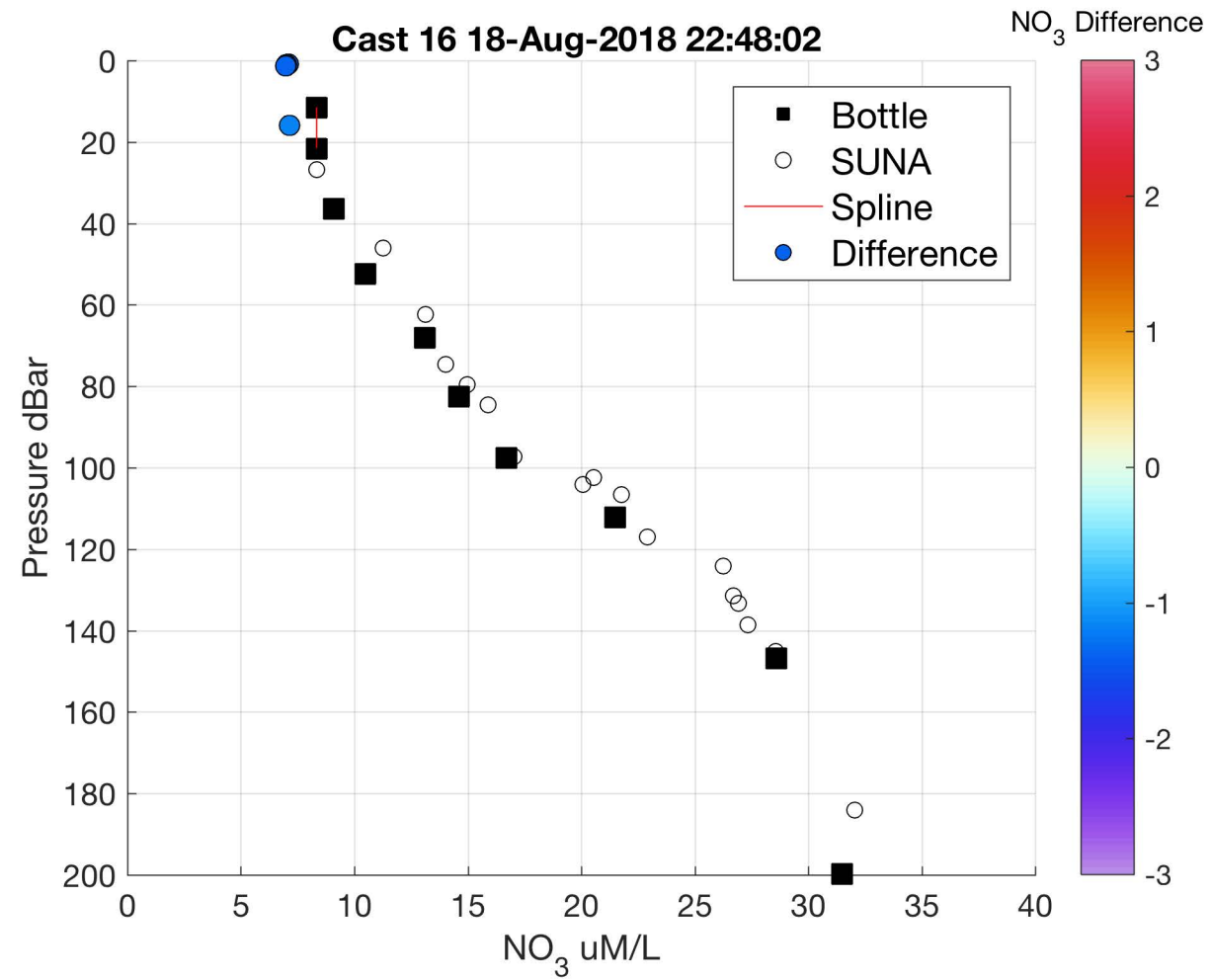
## **APPENDIX C**

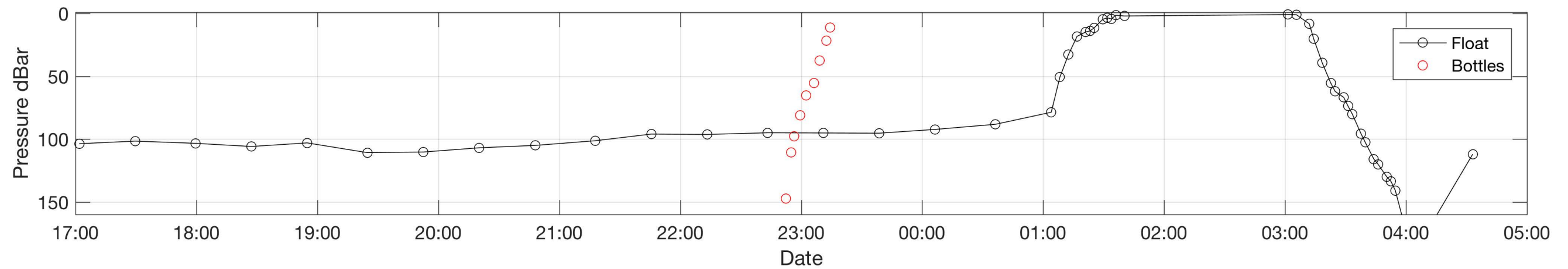
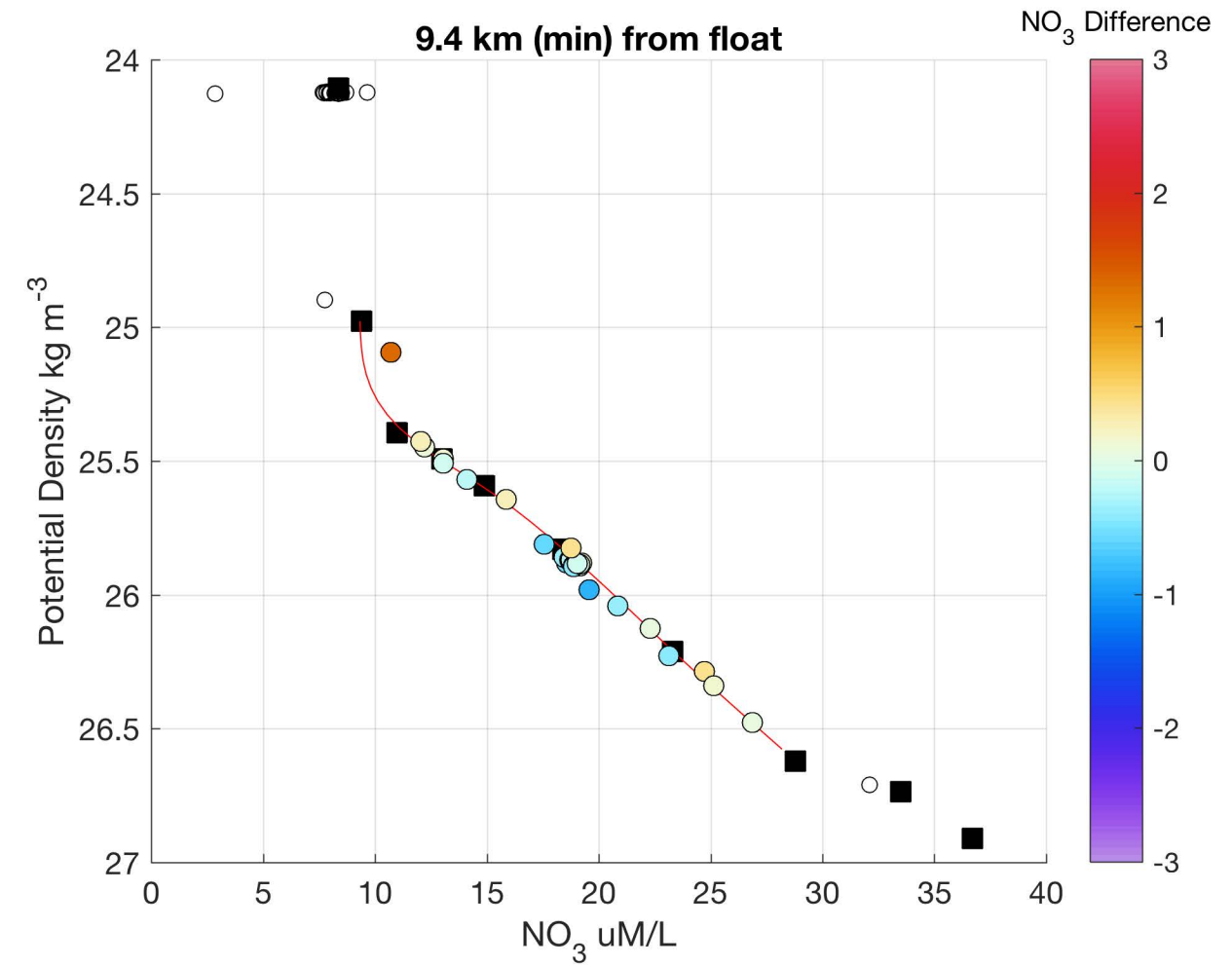
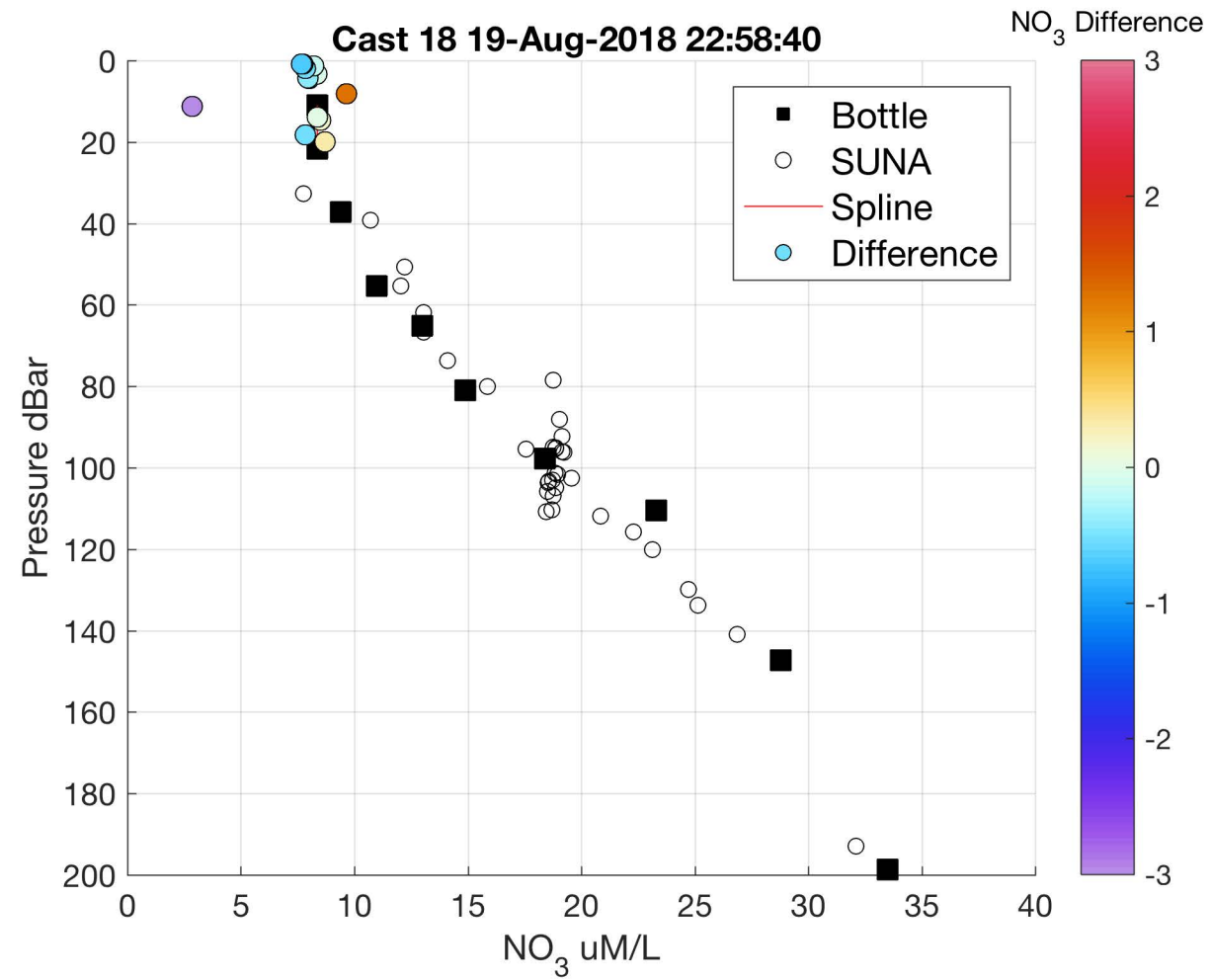


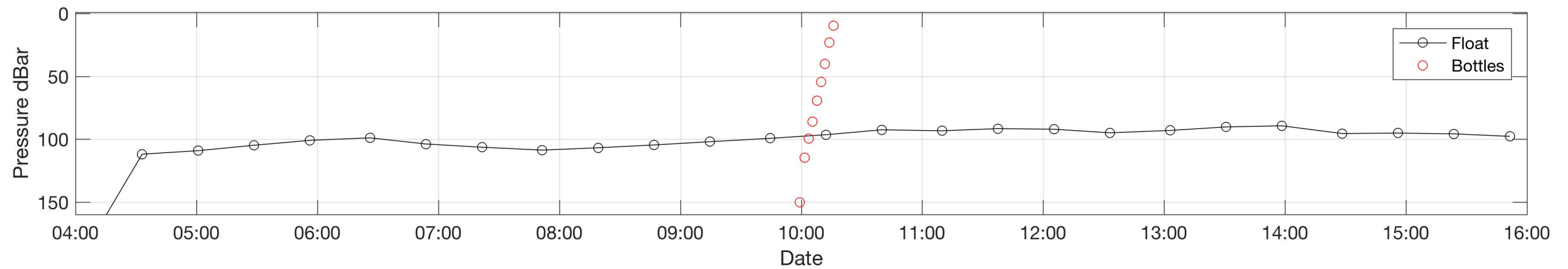
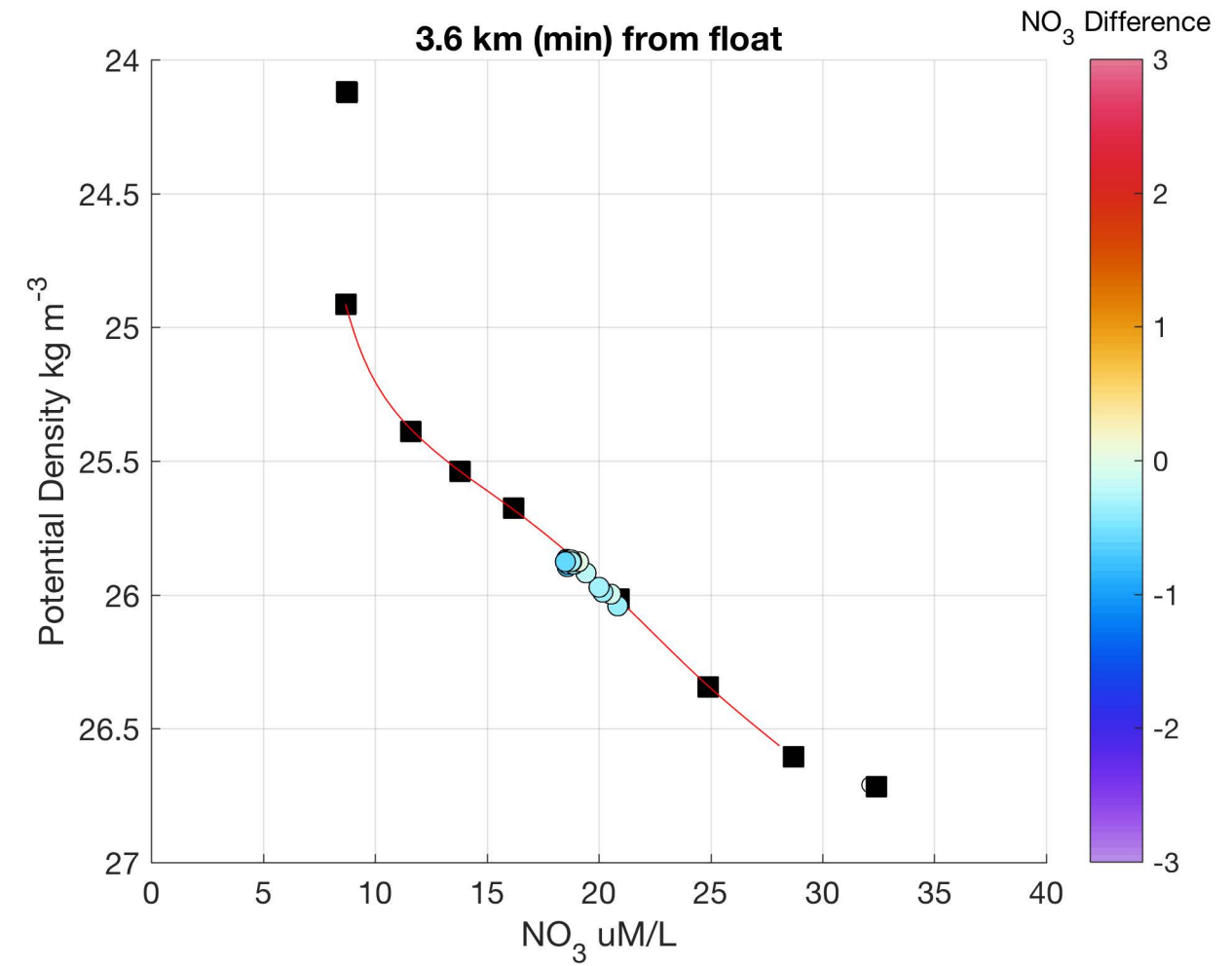
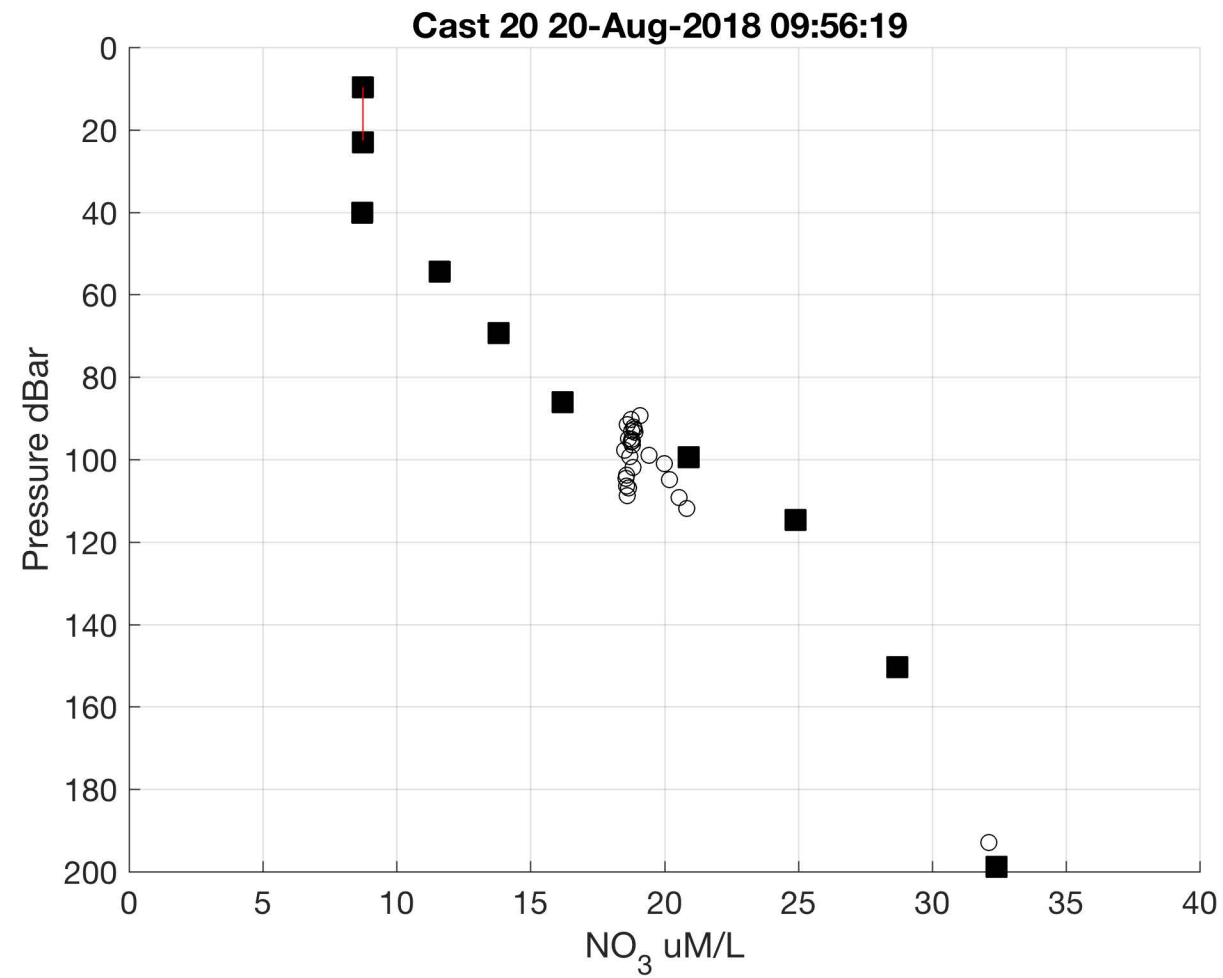


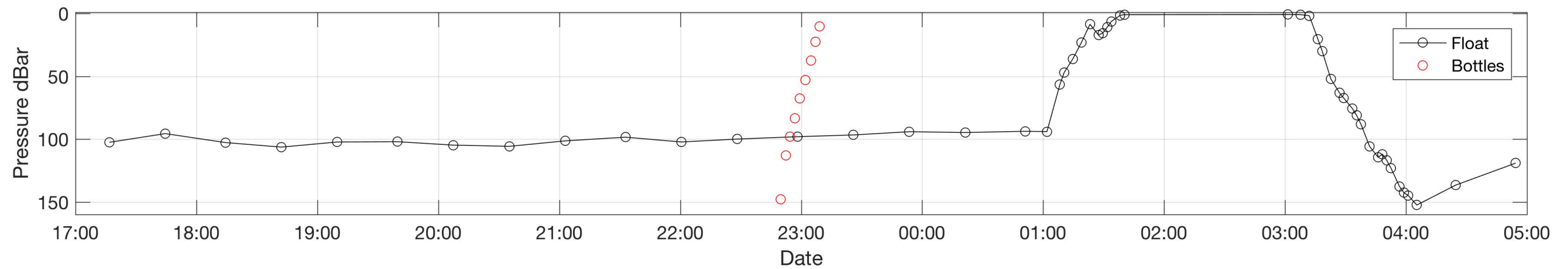
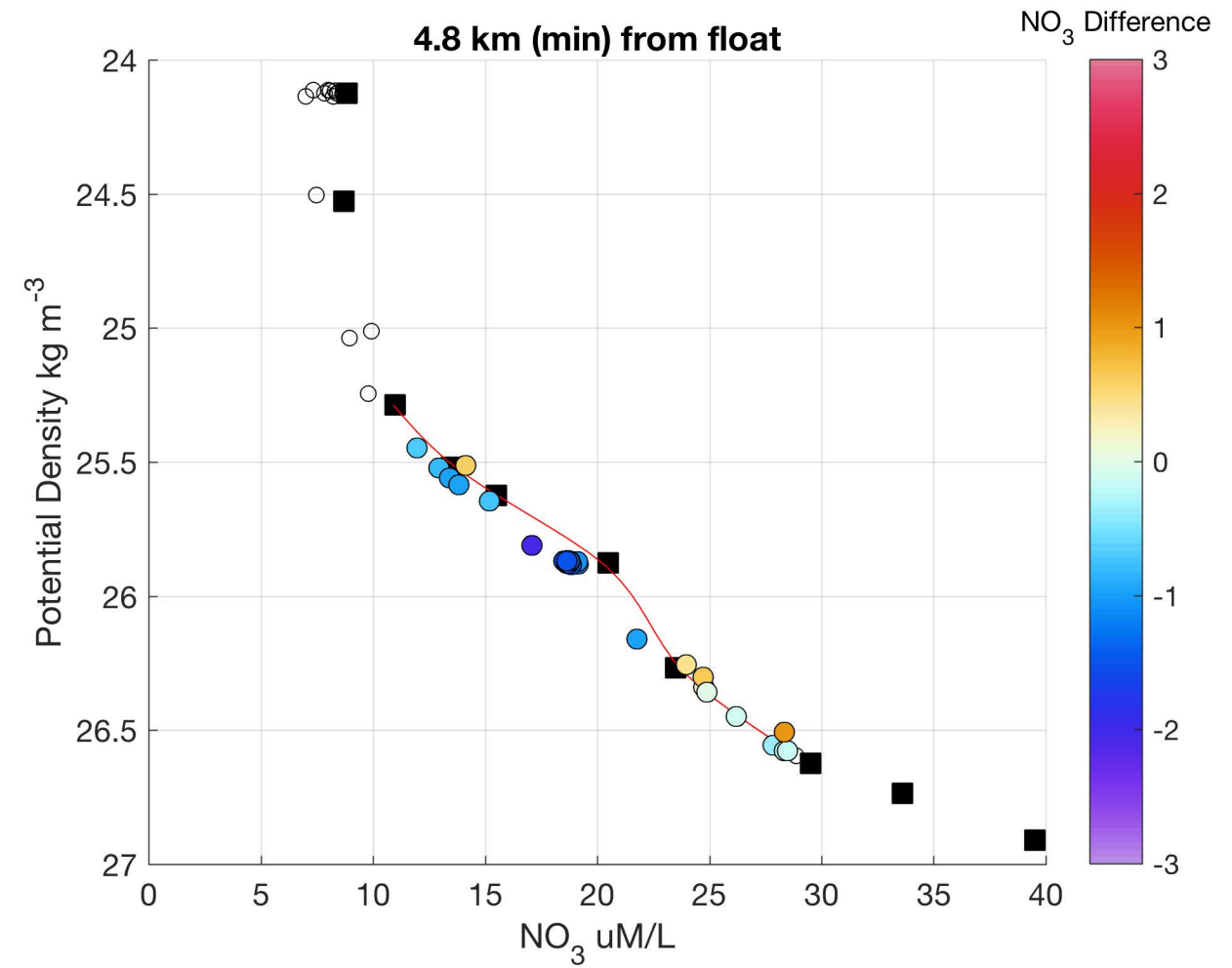
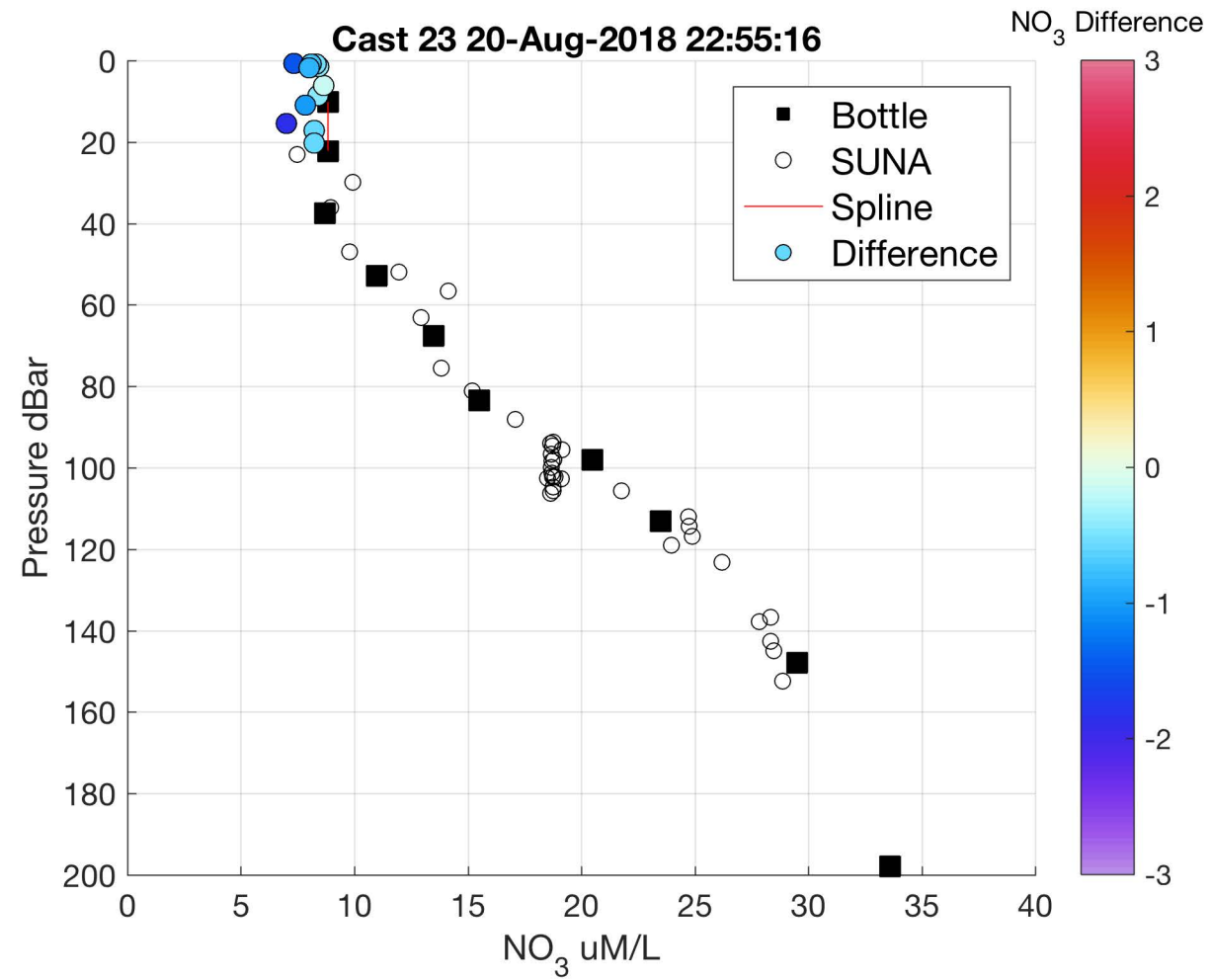




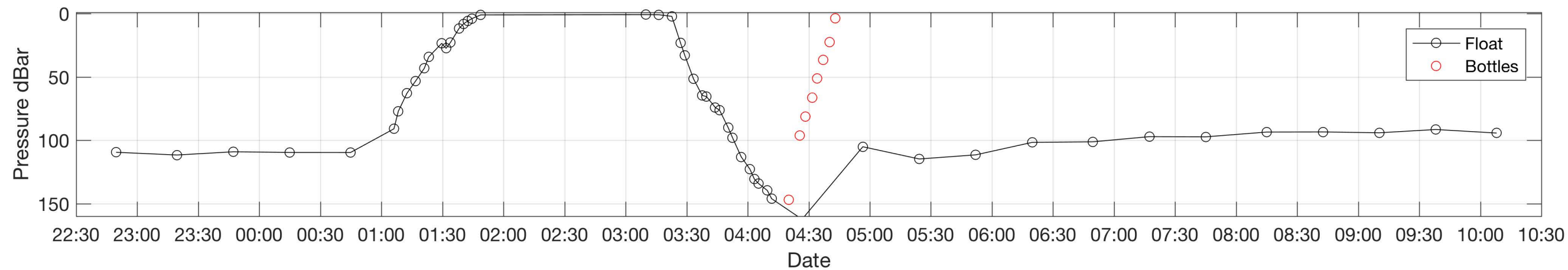
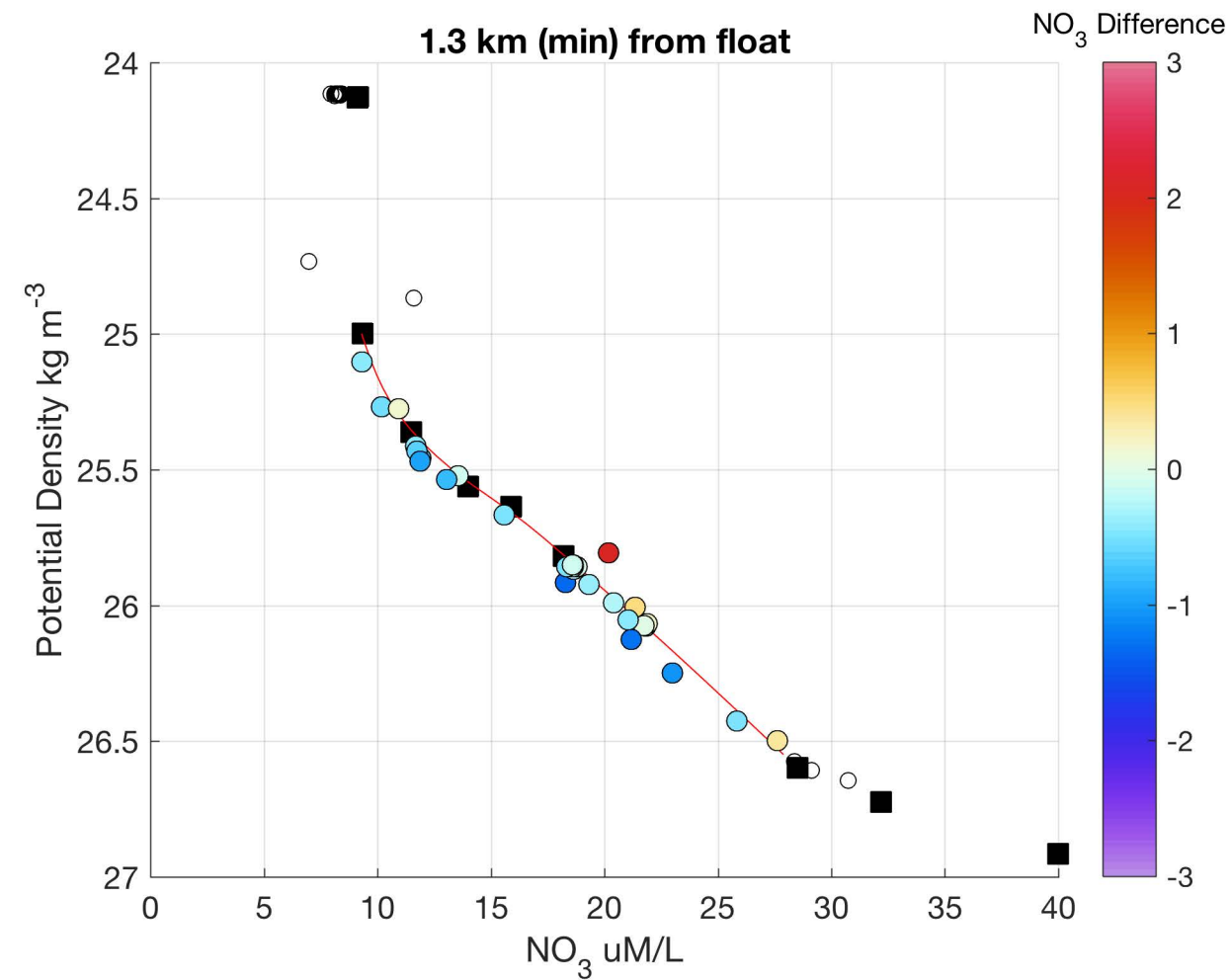
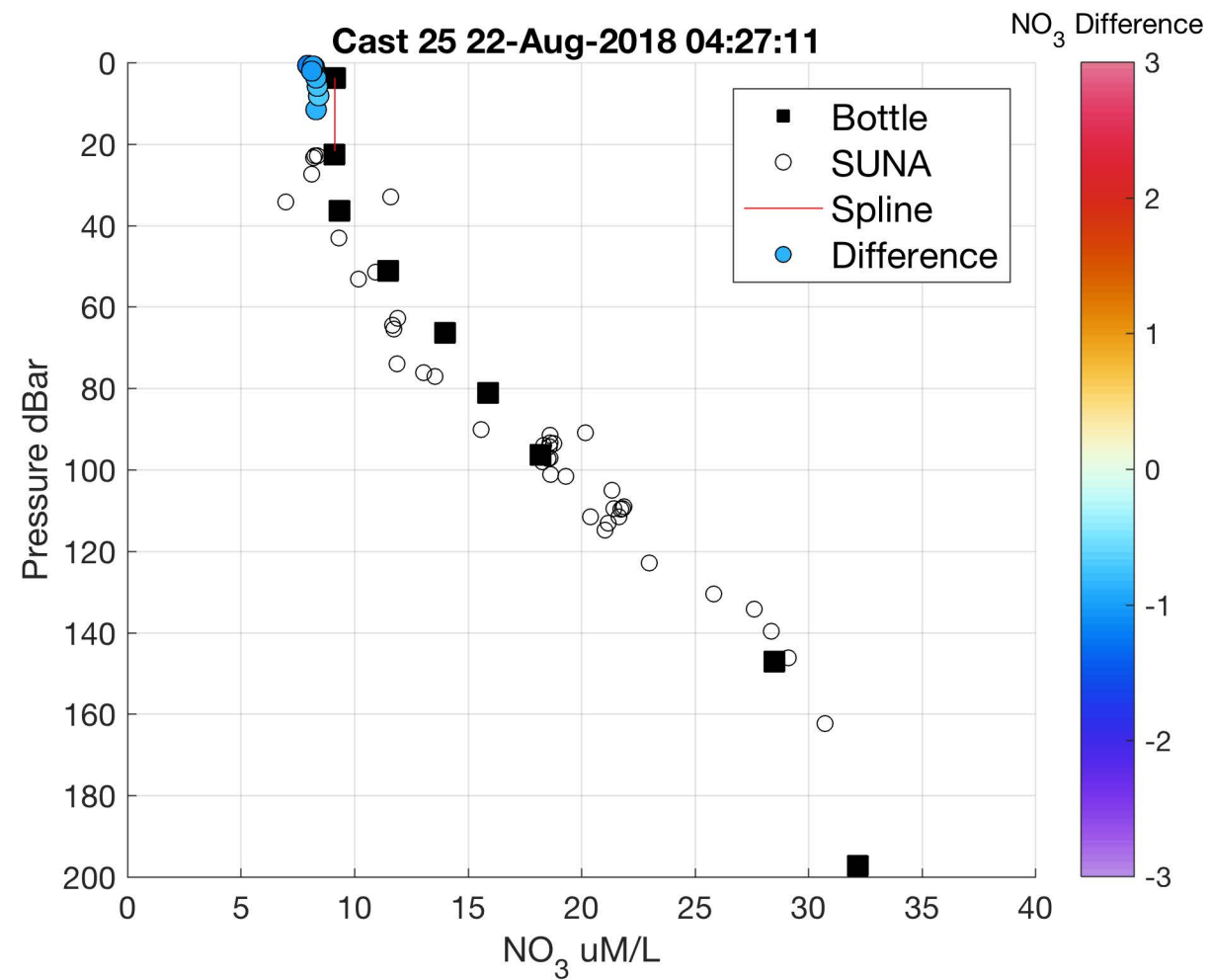


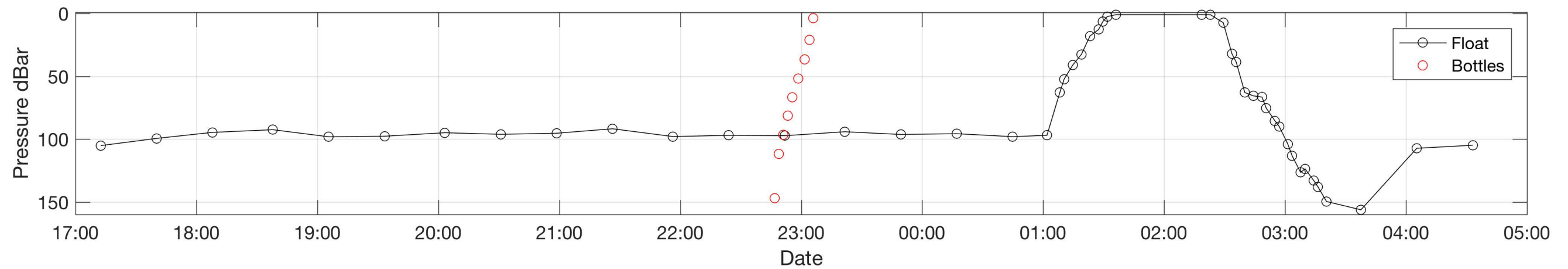
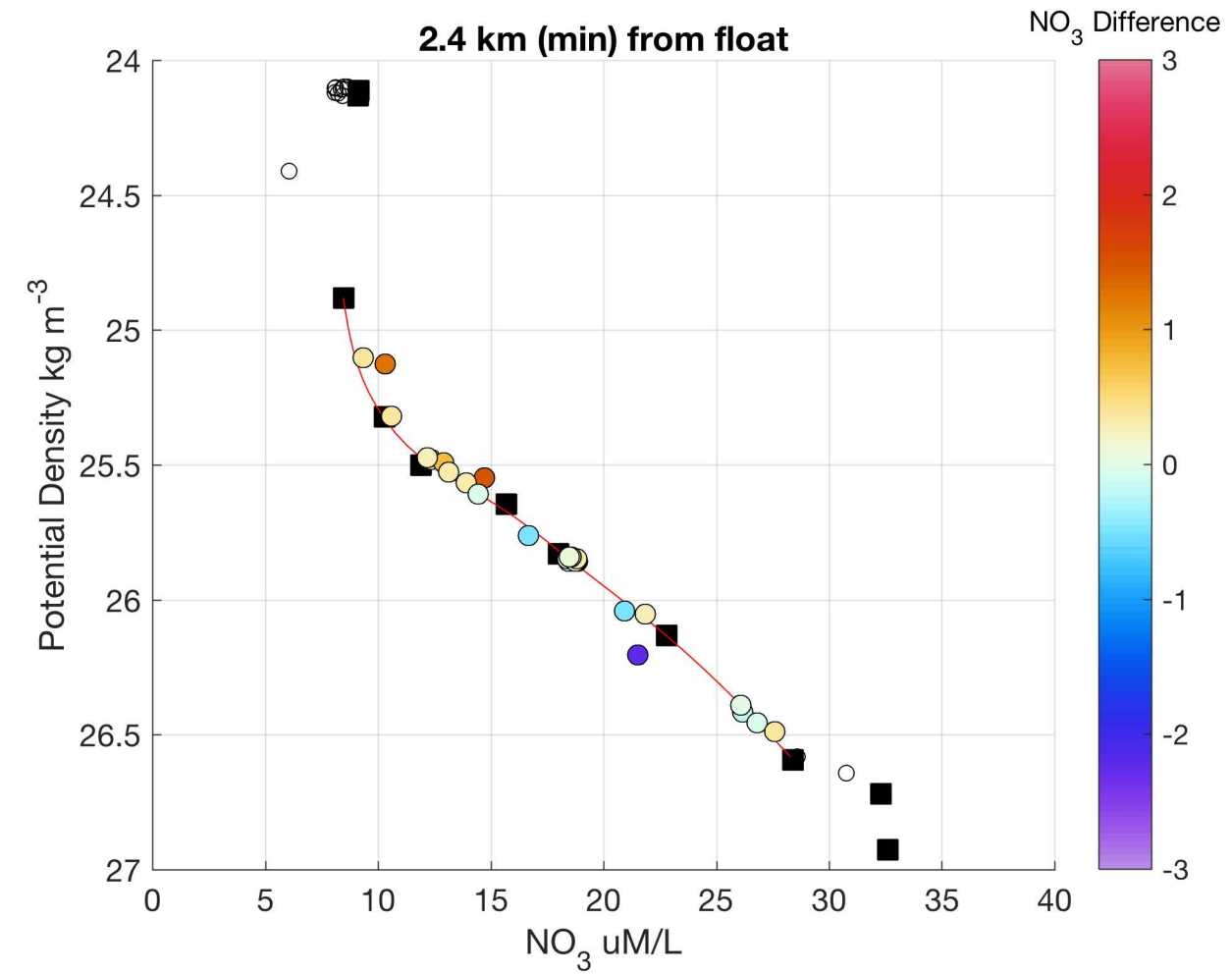
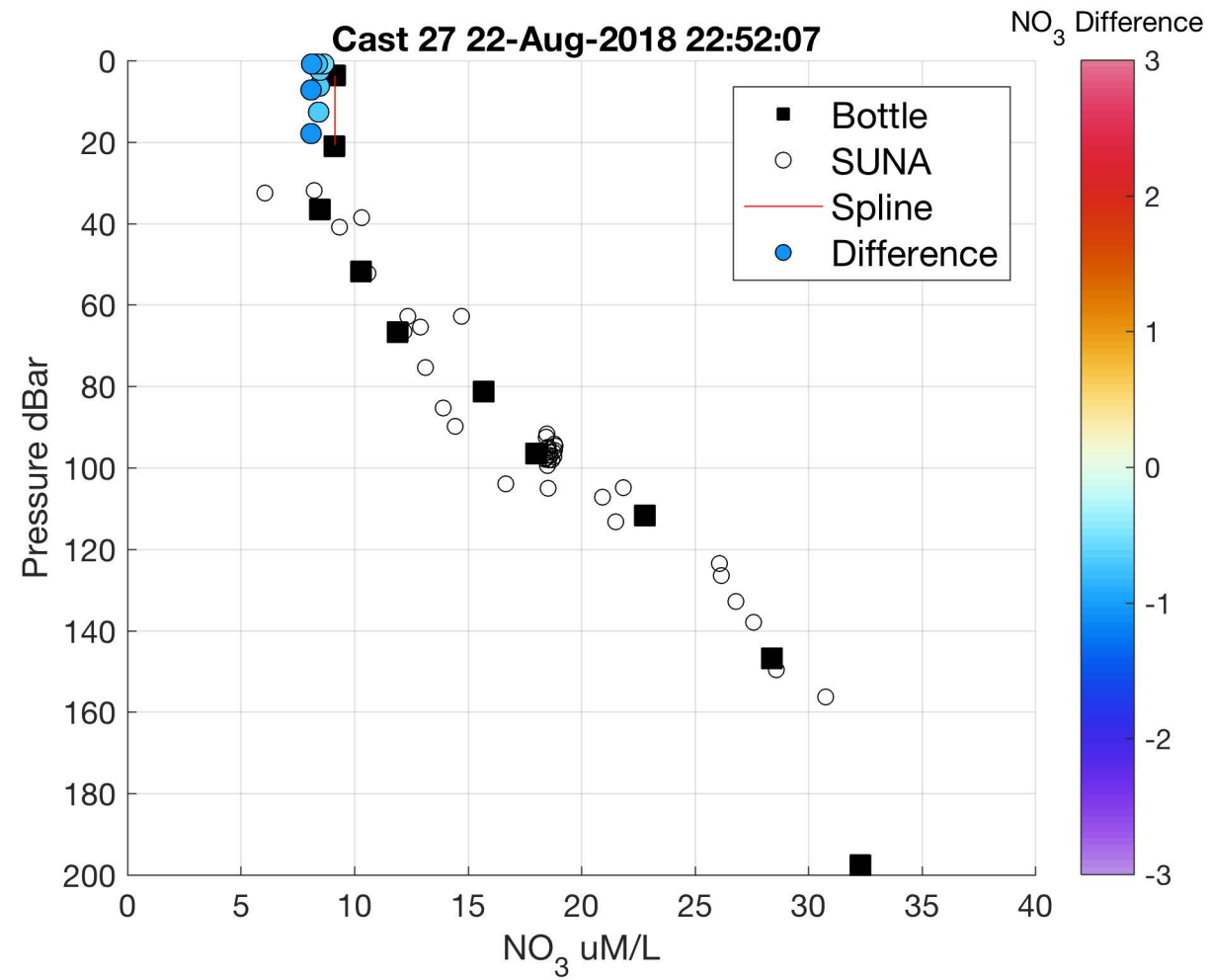


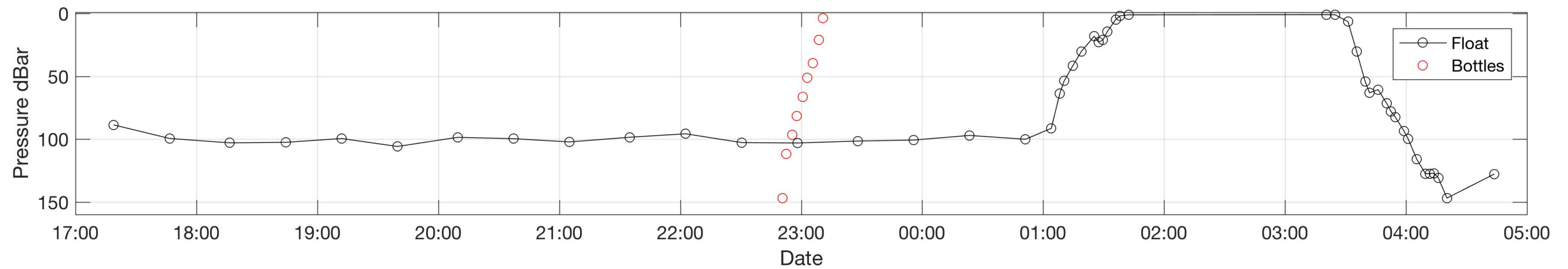
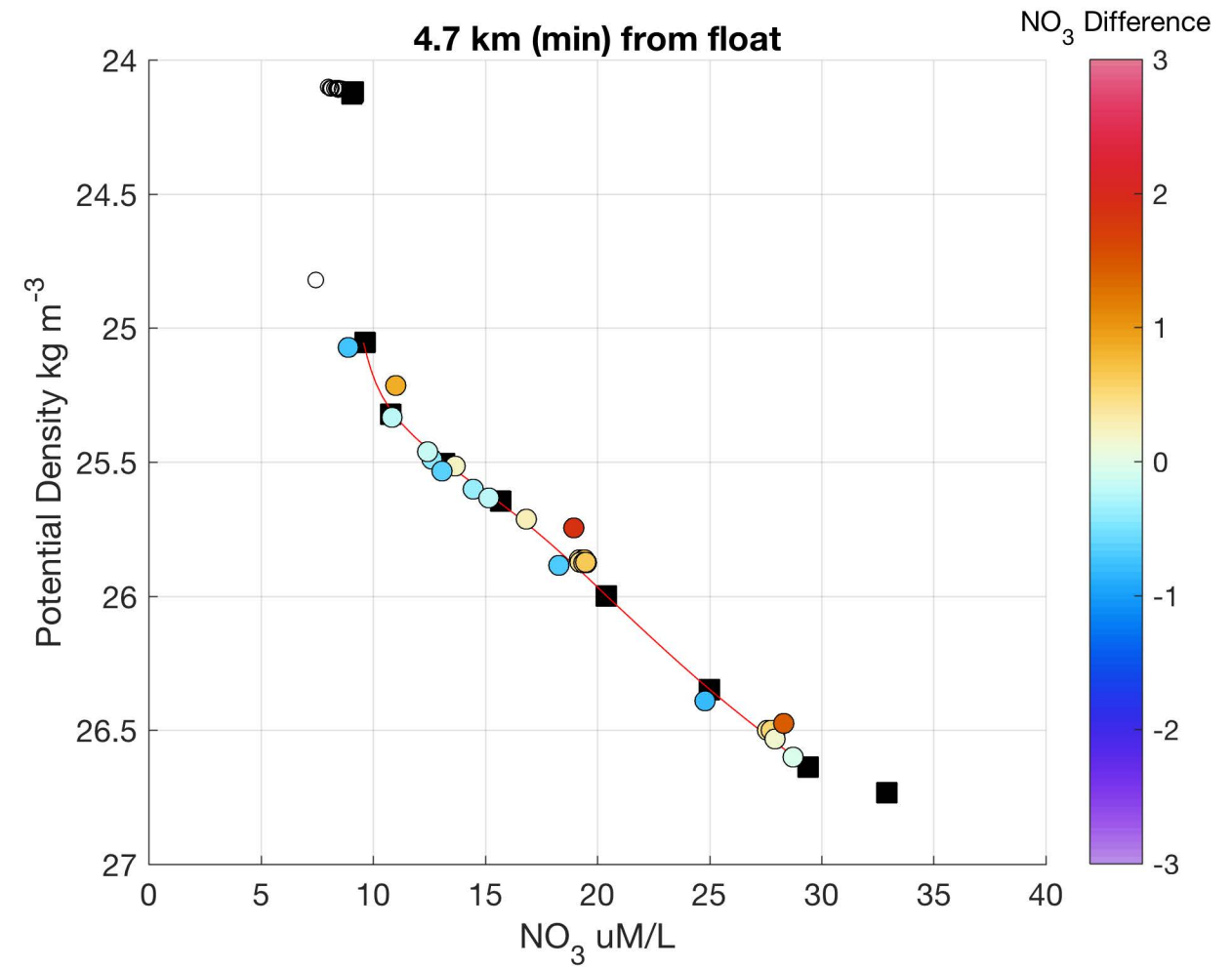
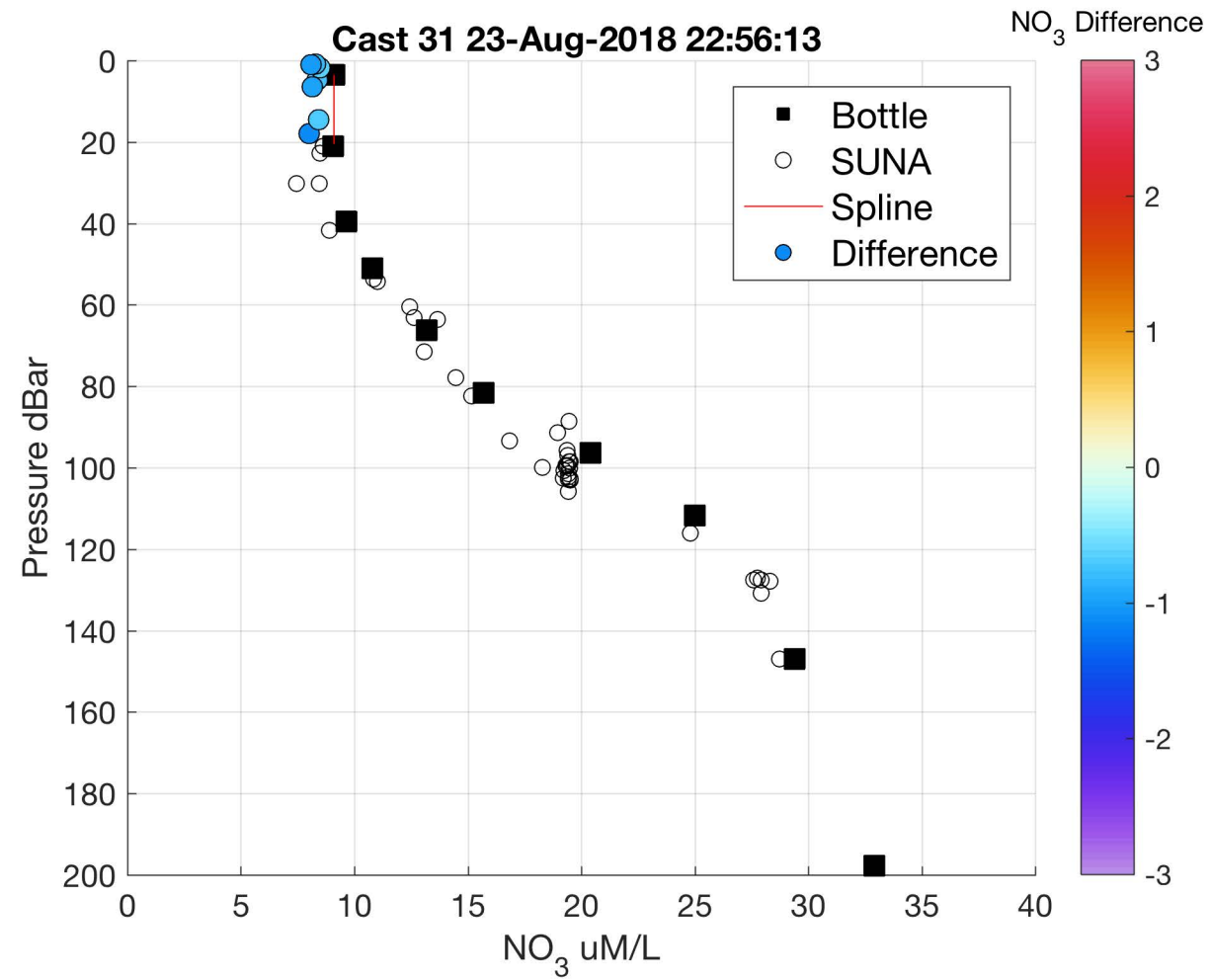


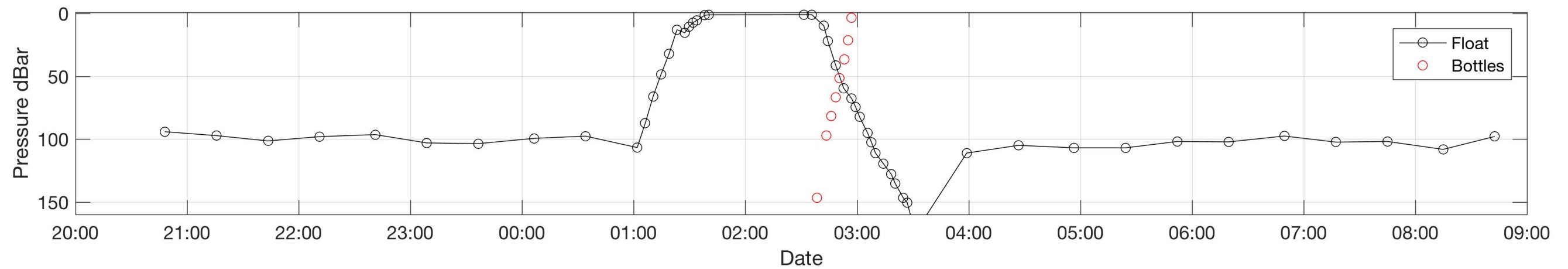
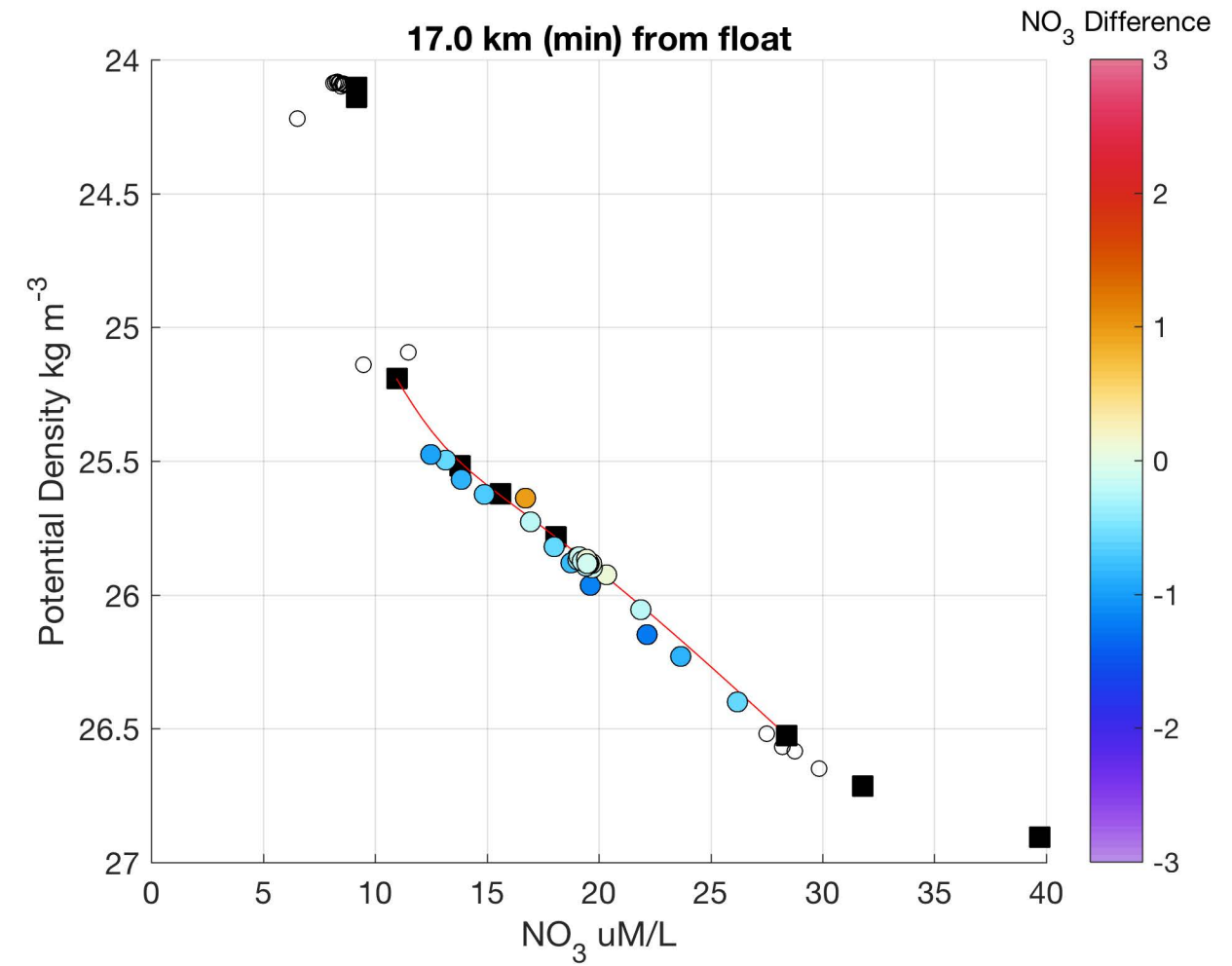
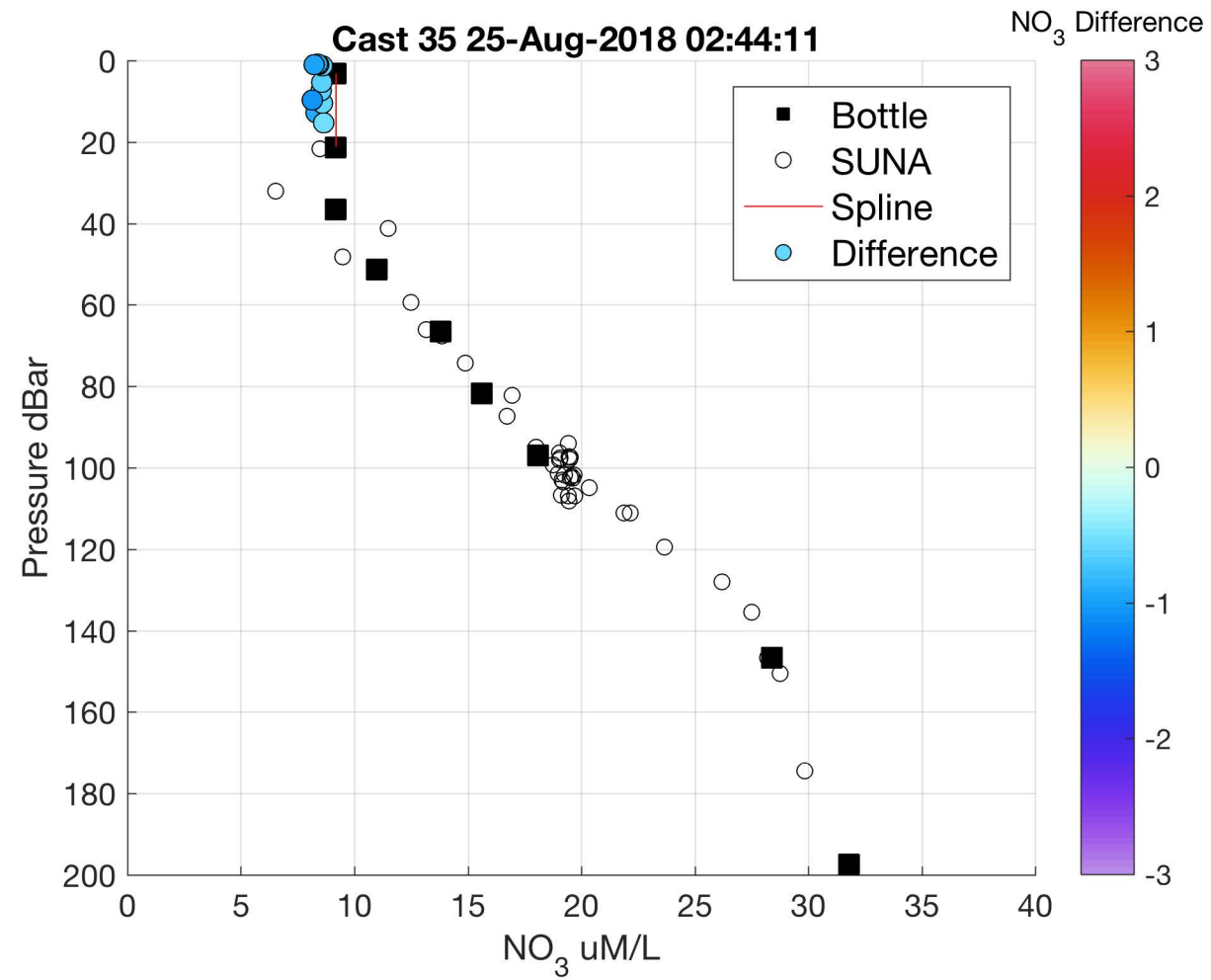


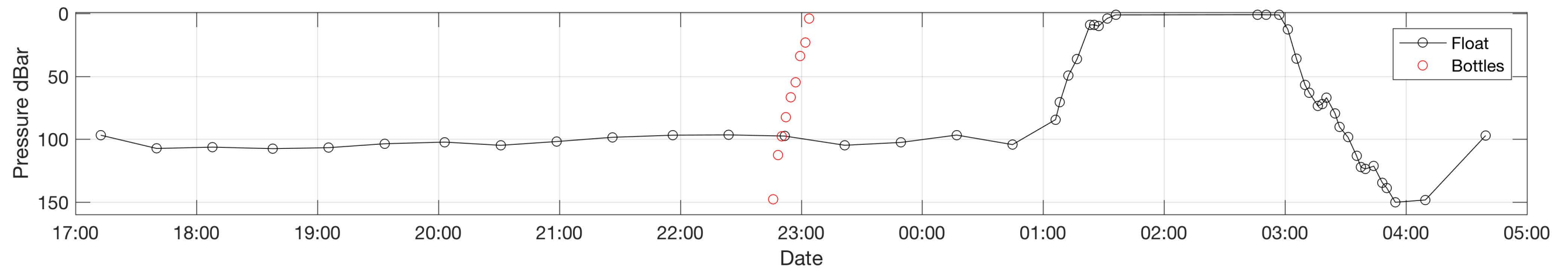
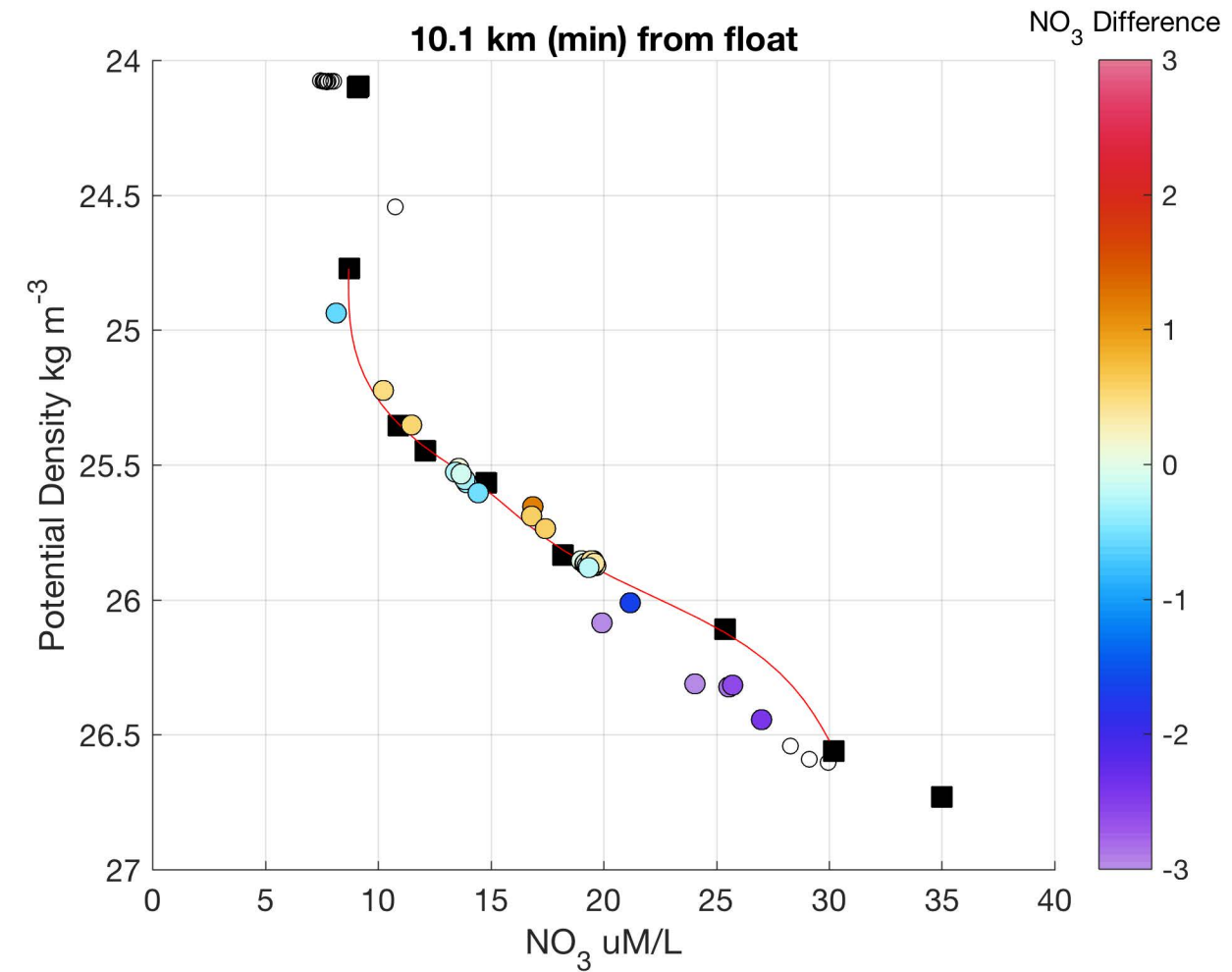
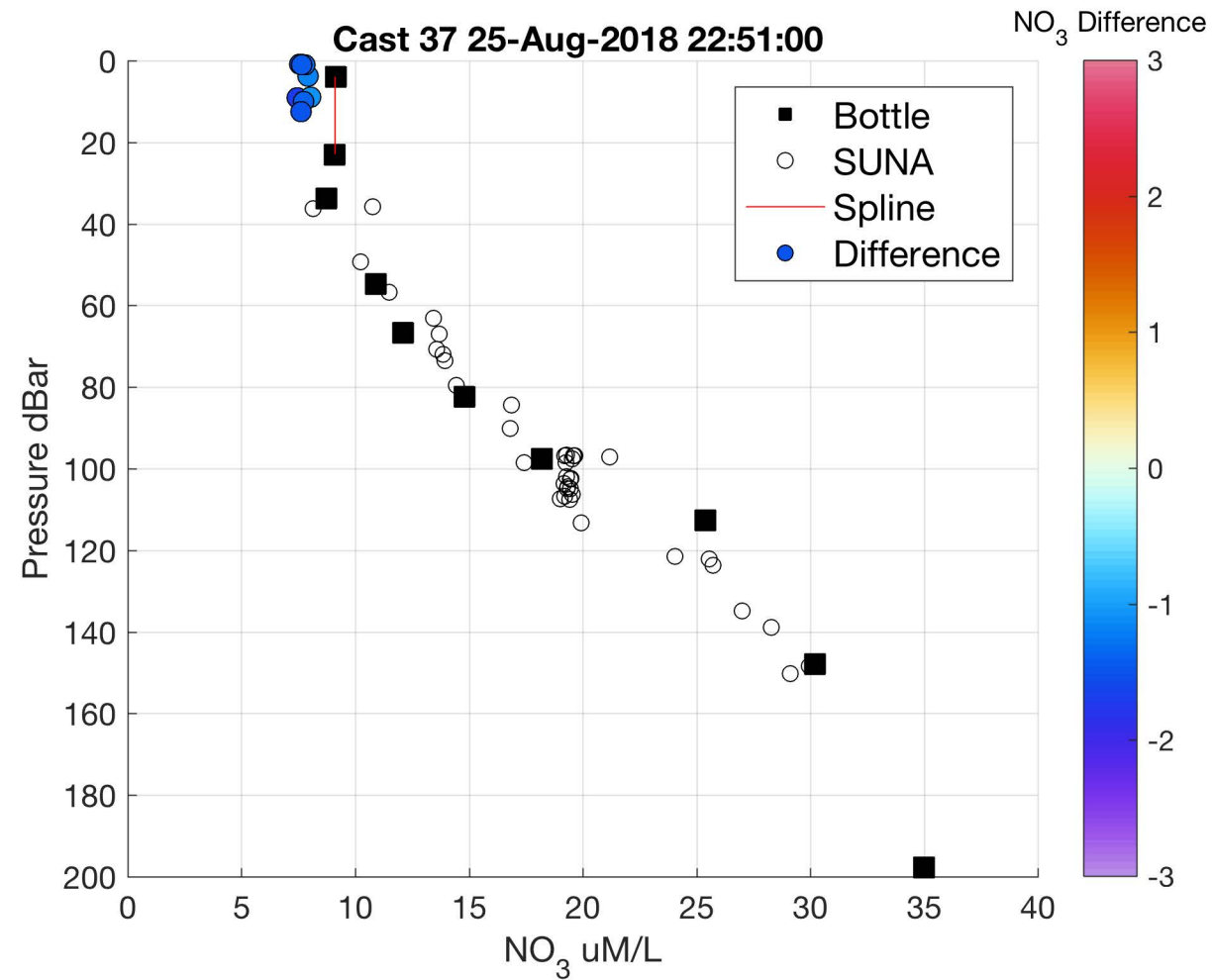


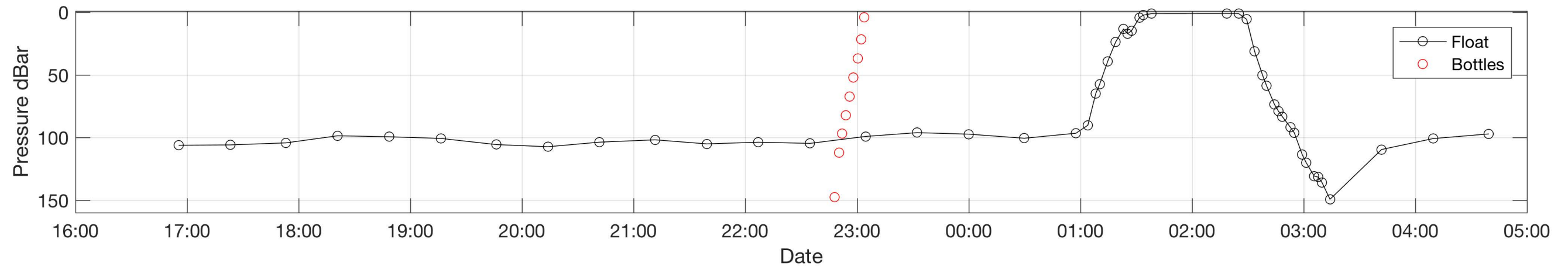
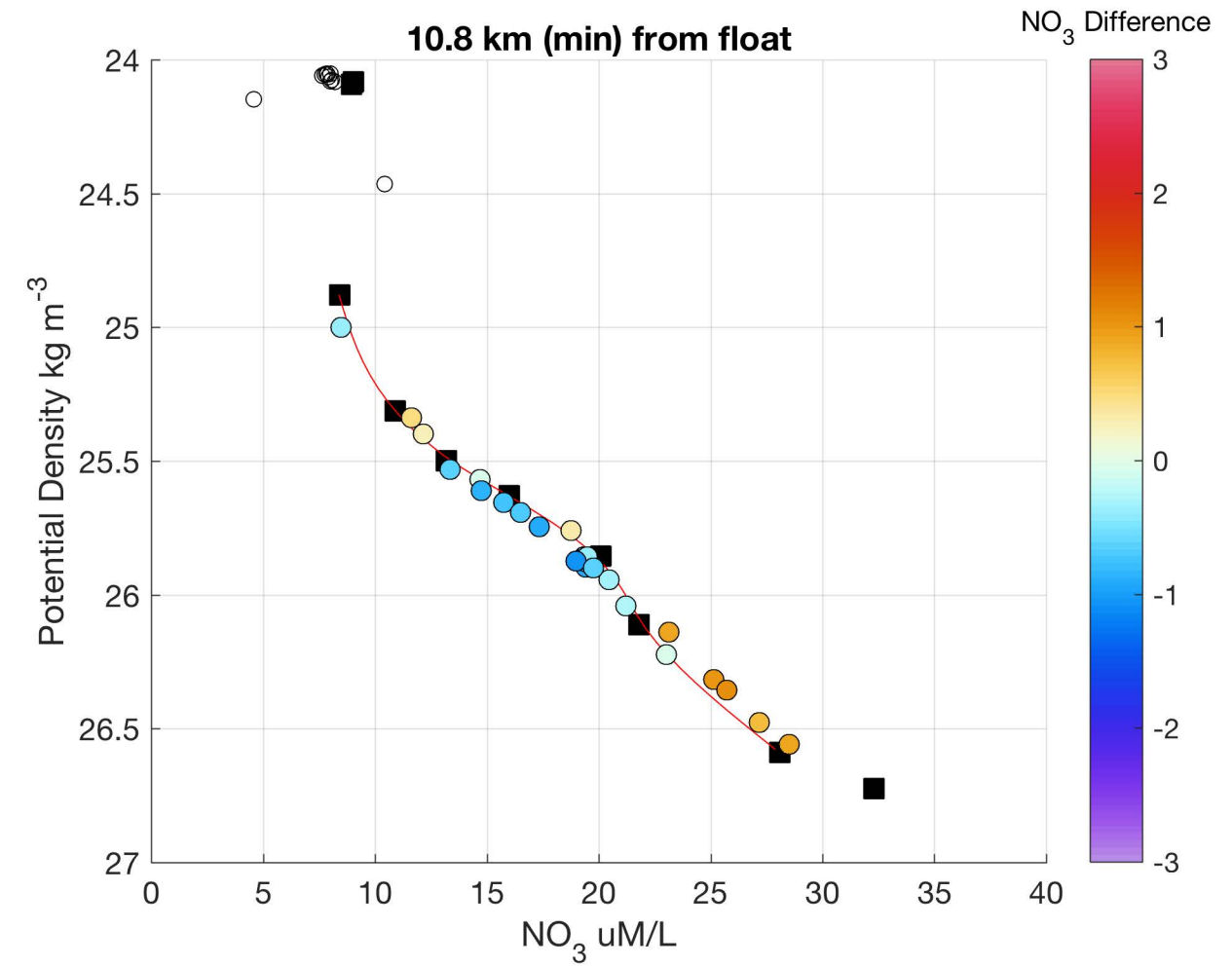
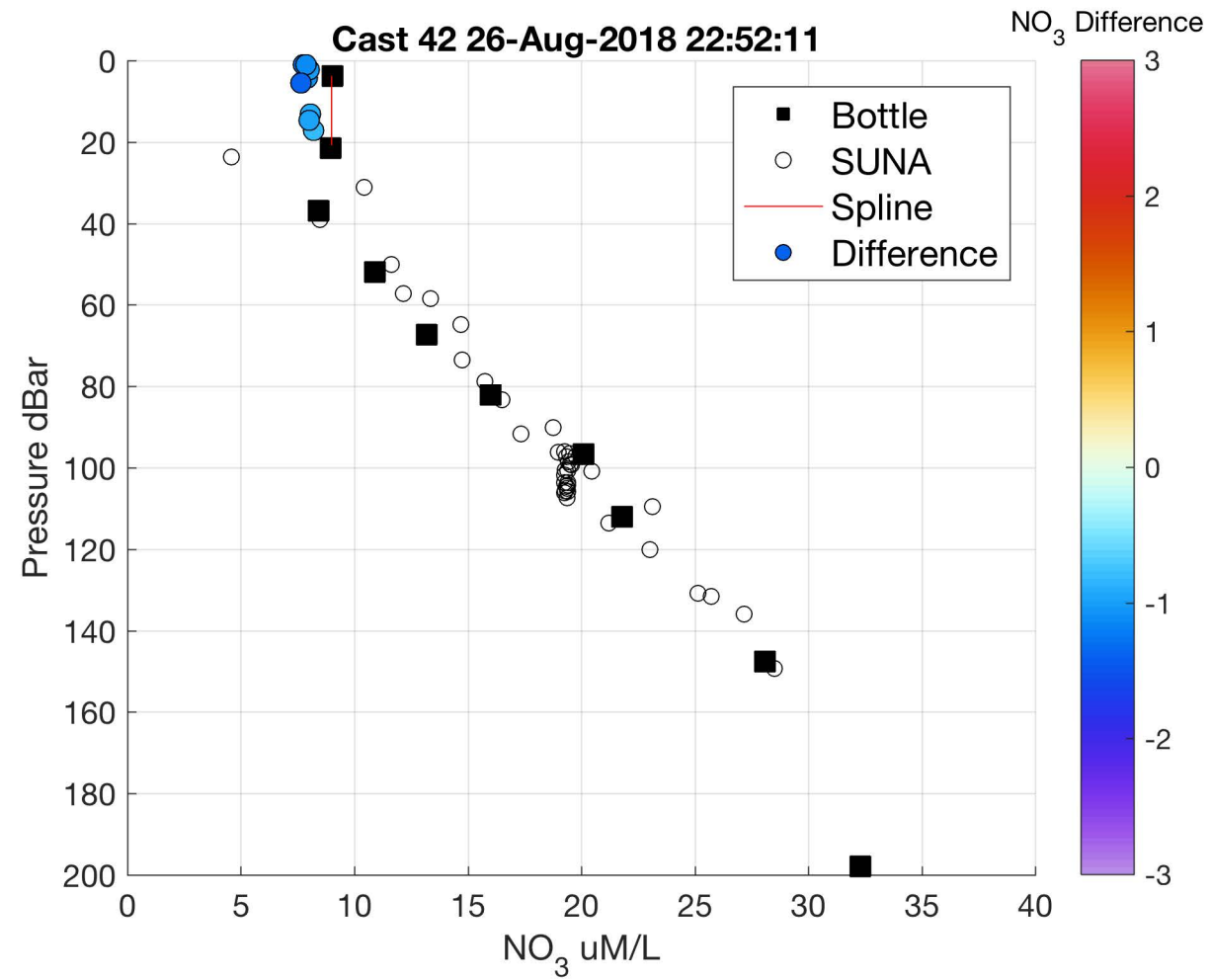


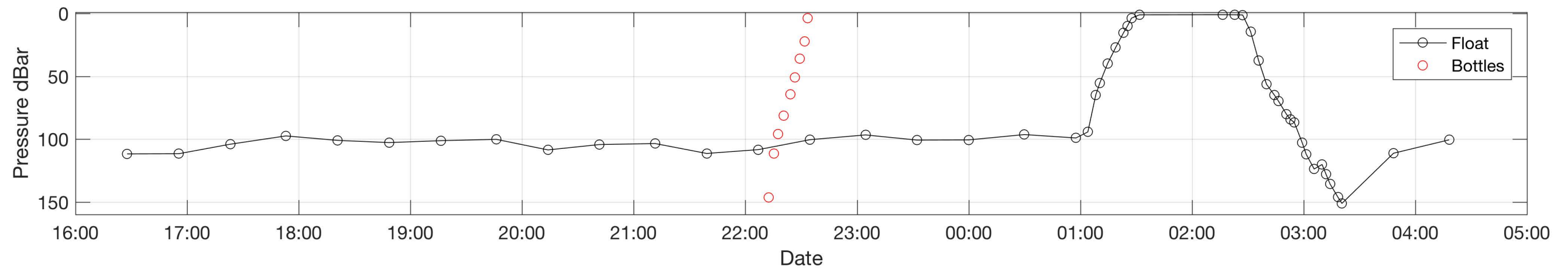
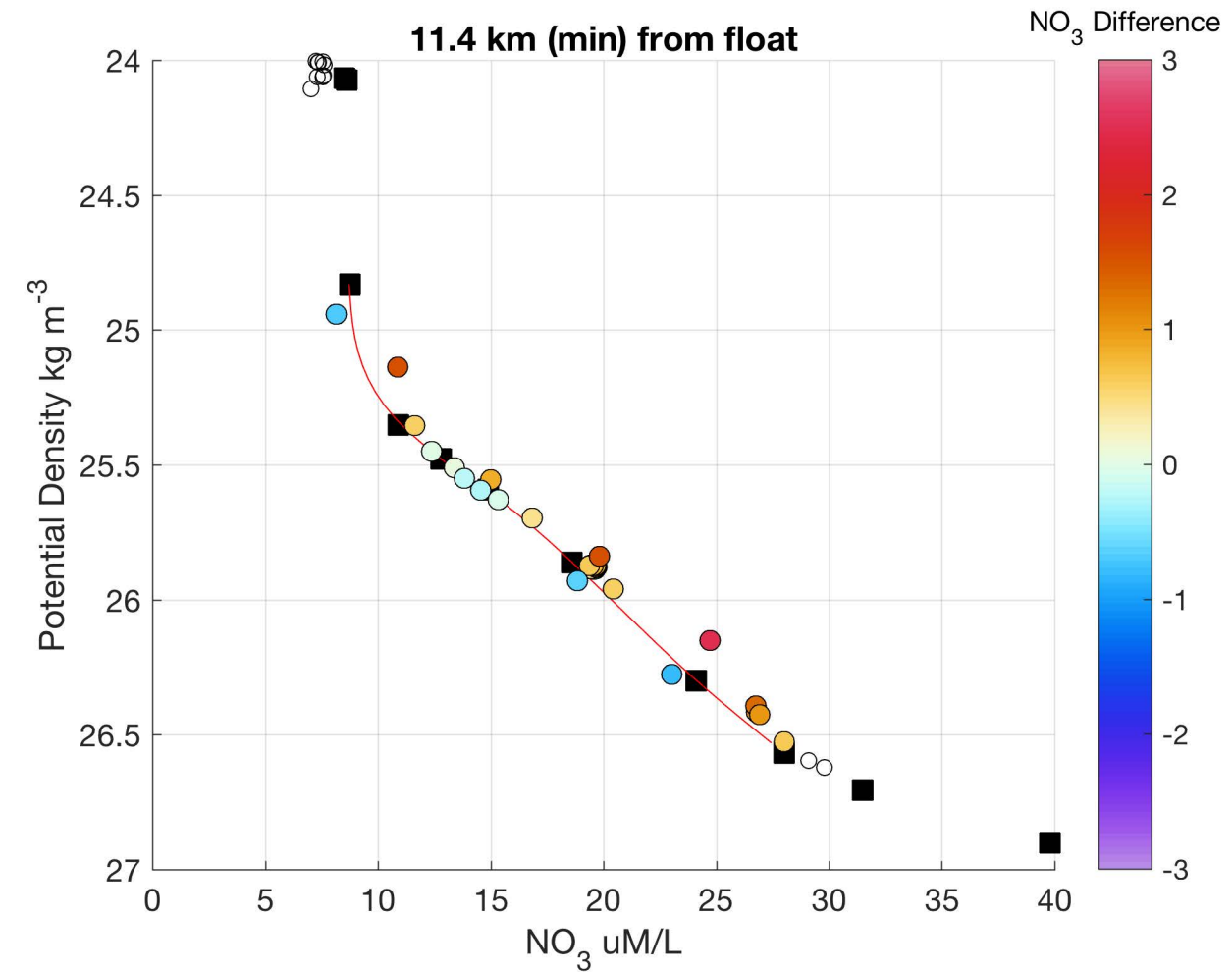
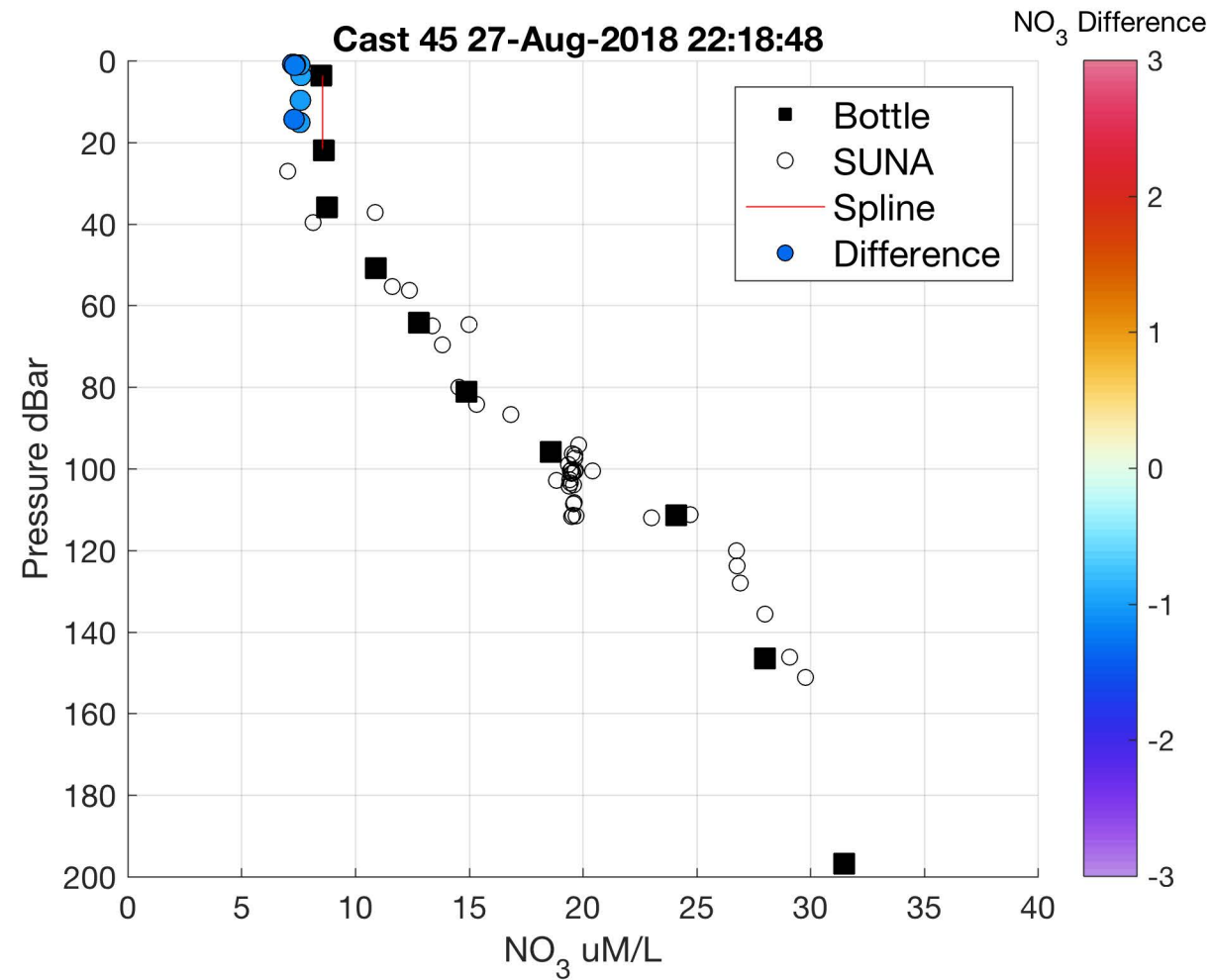




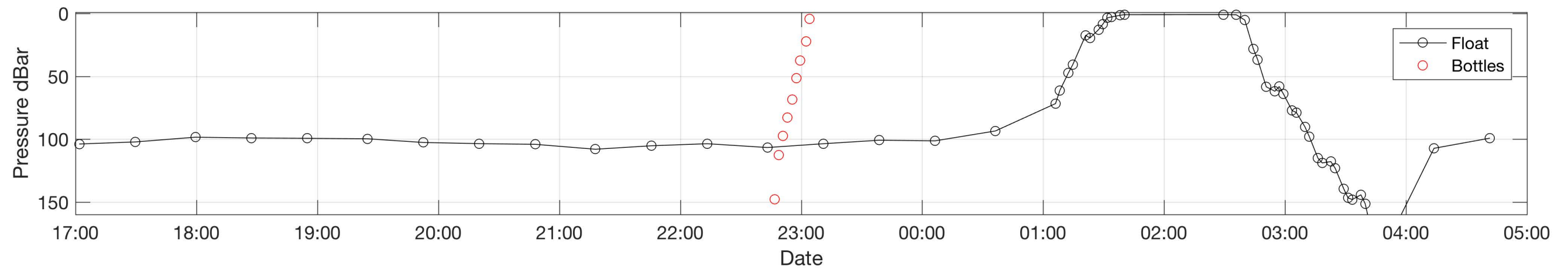
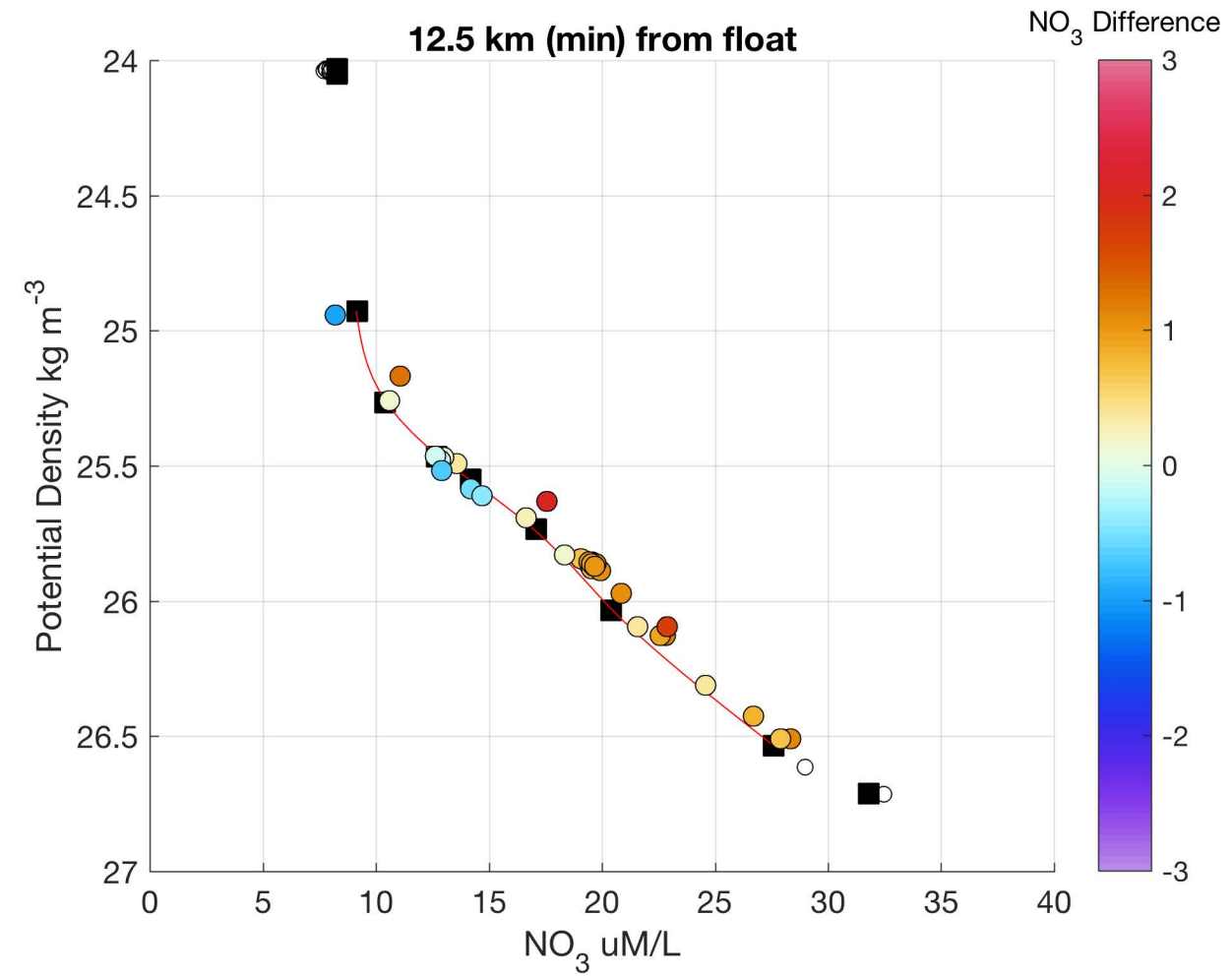
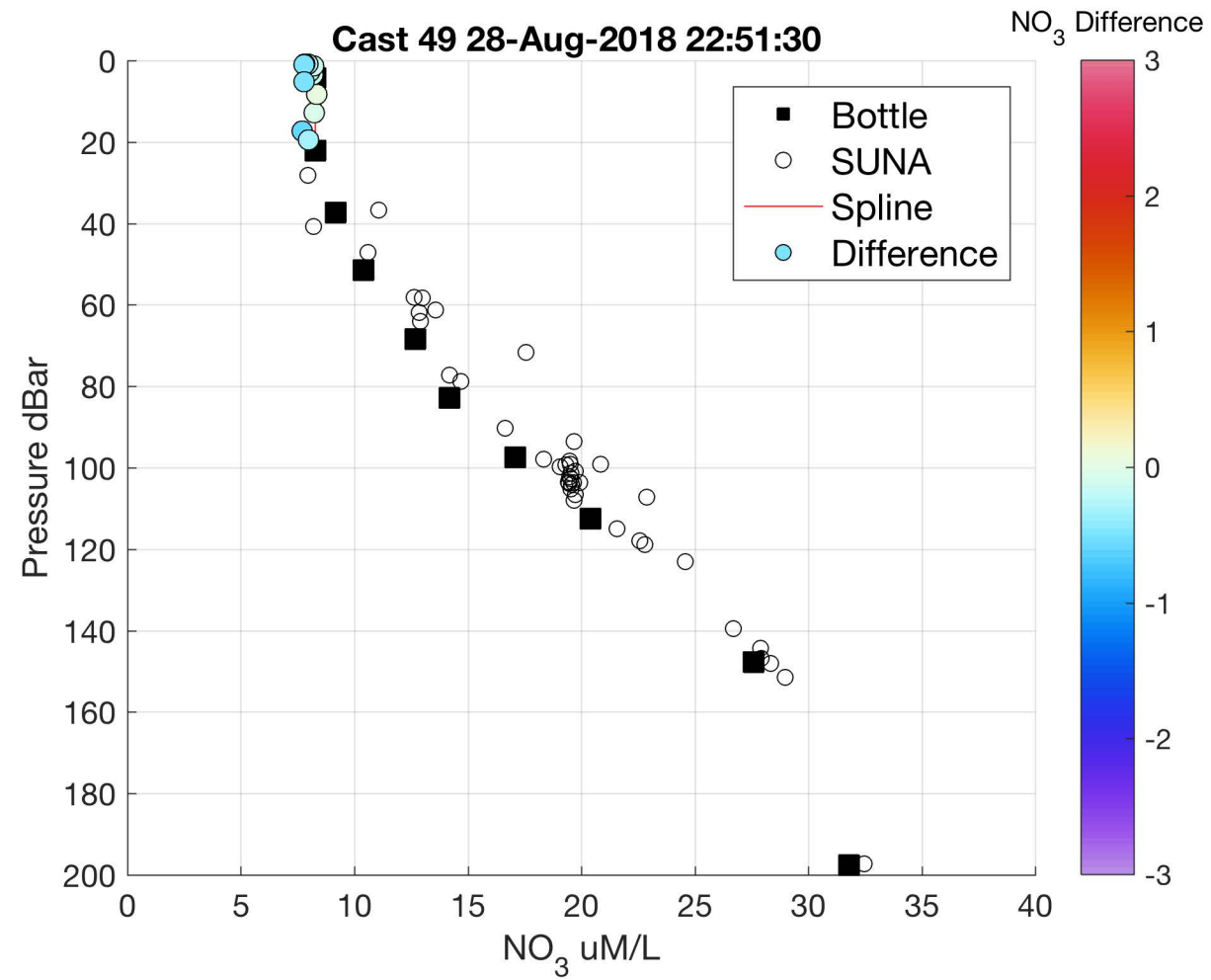


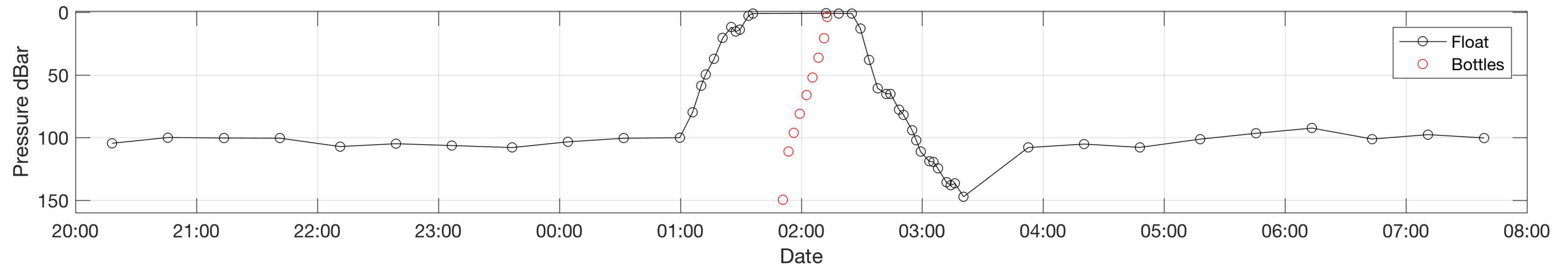
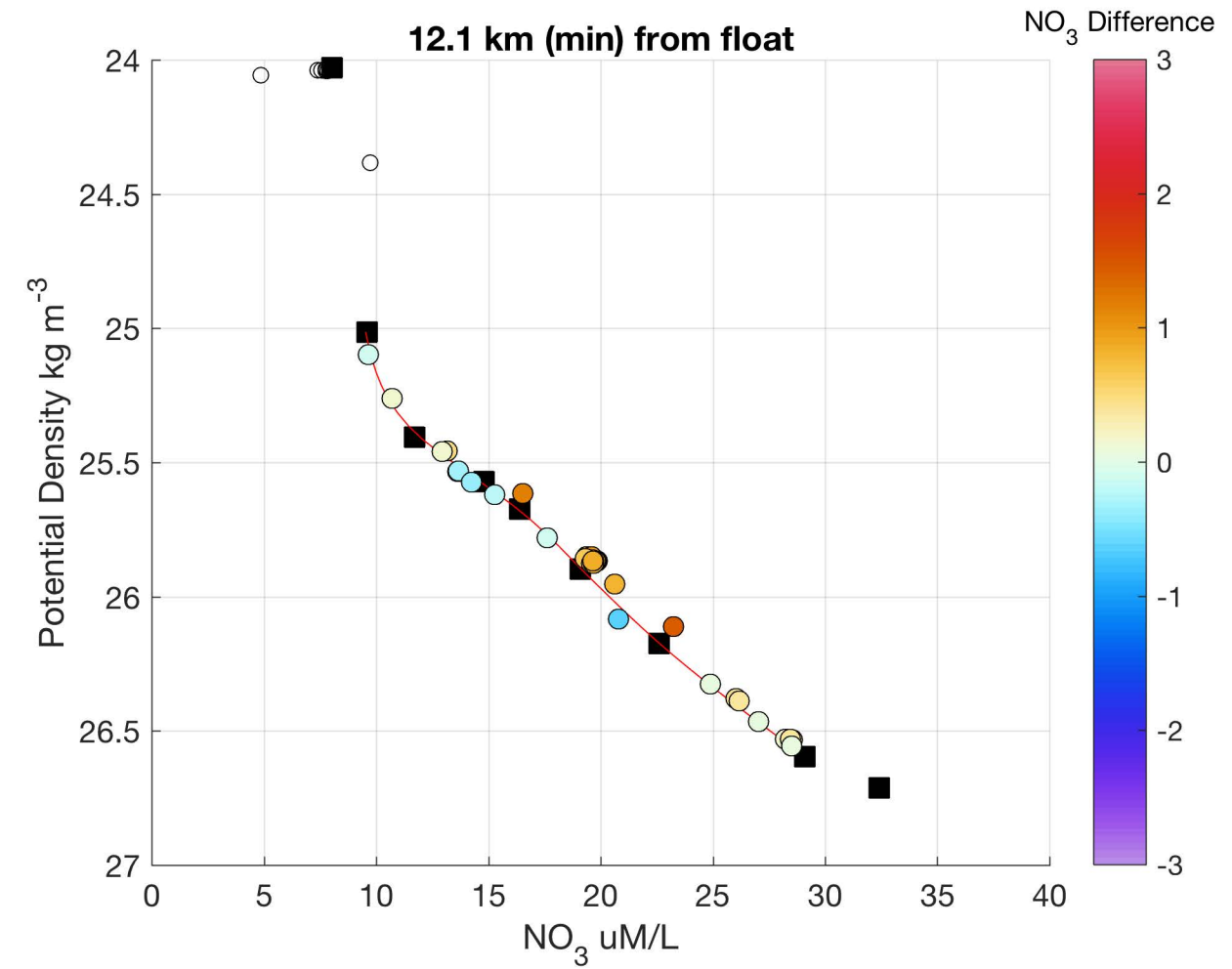
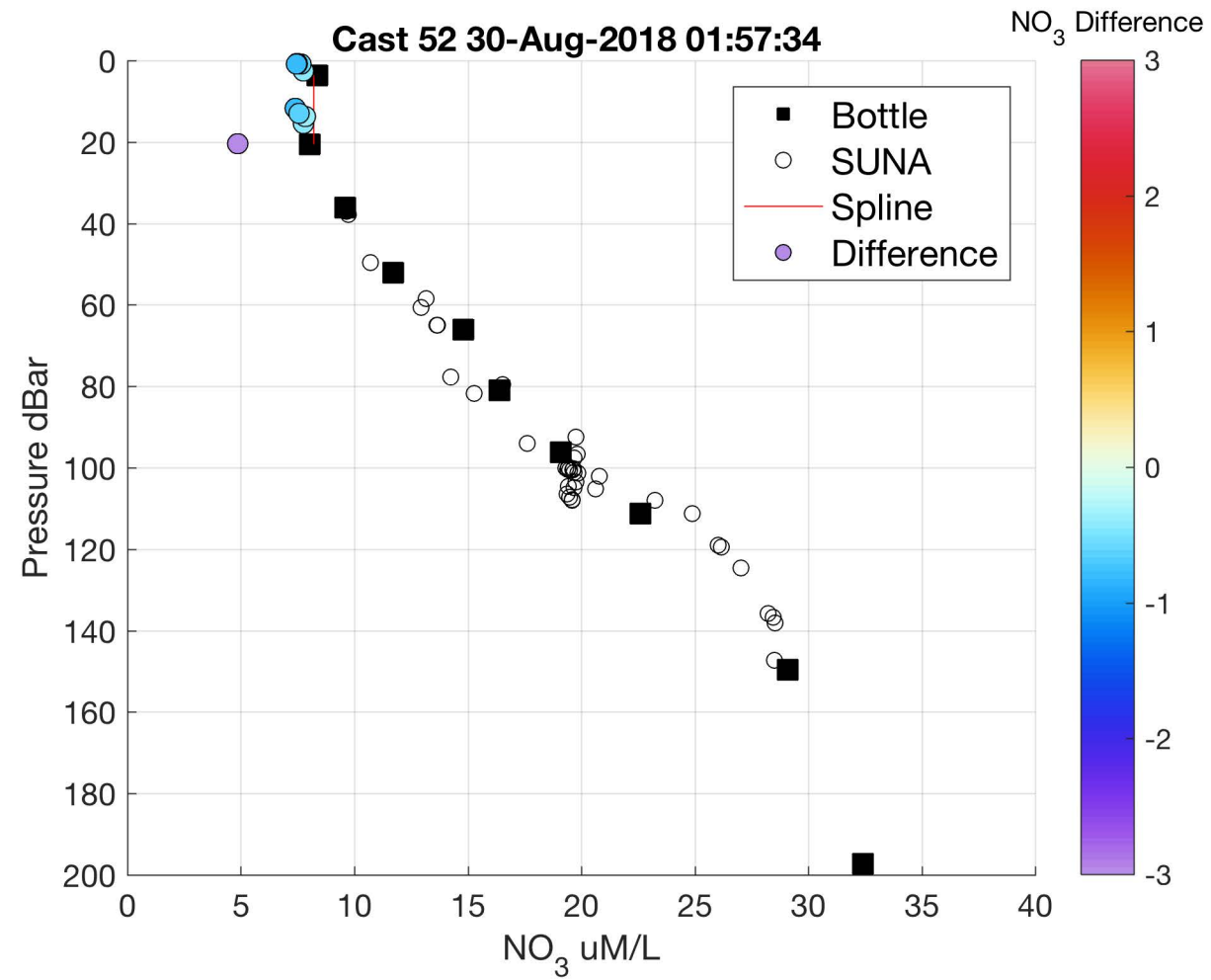


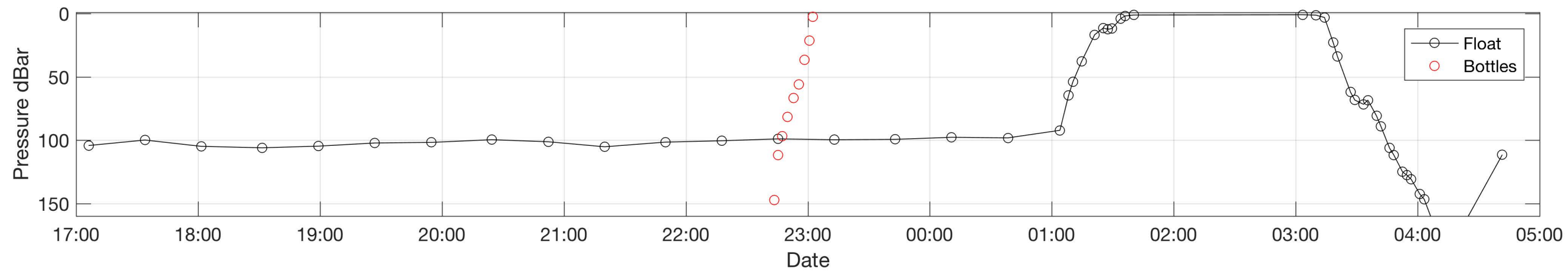
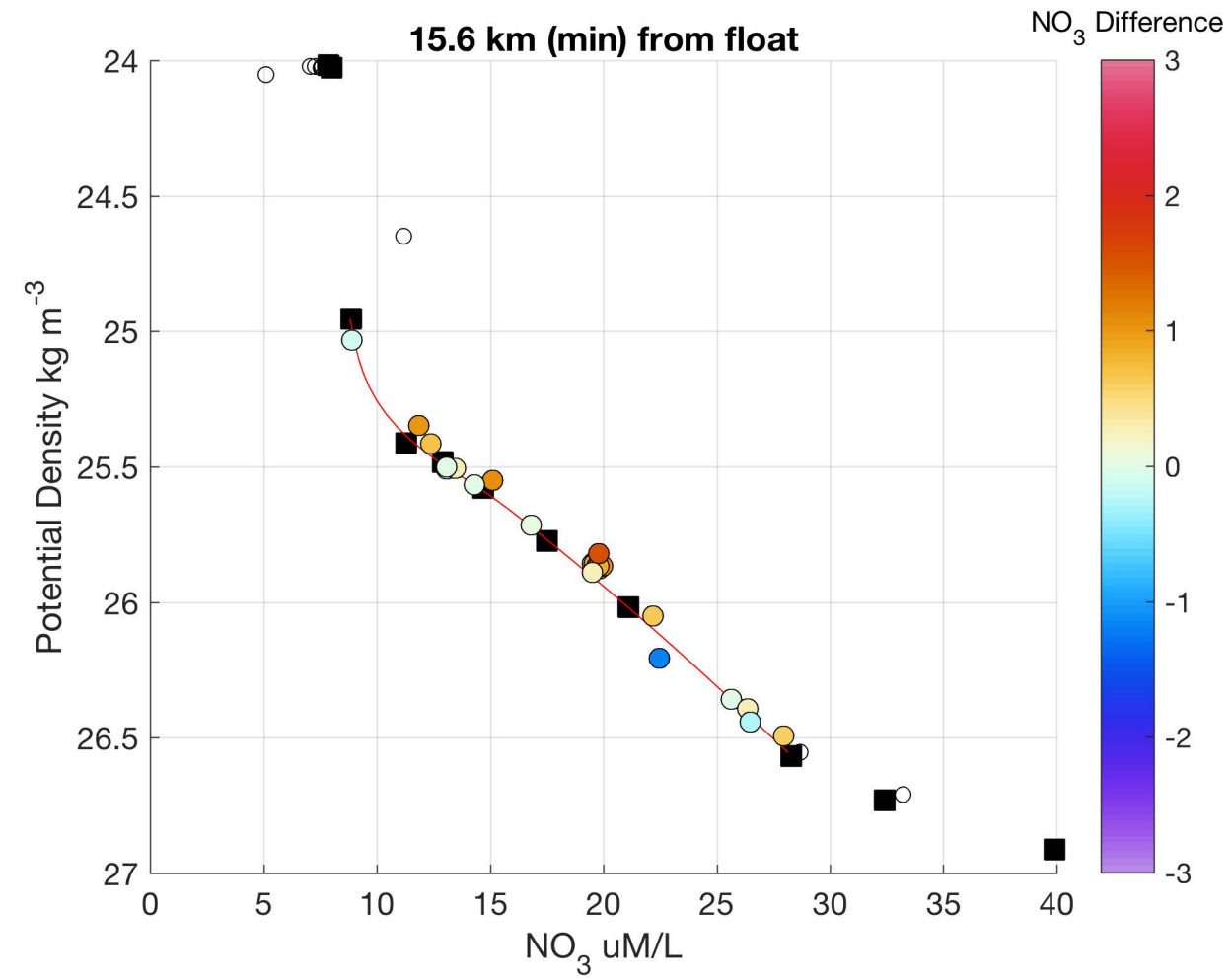
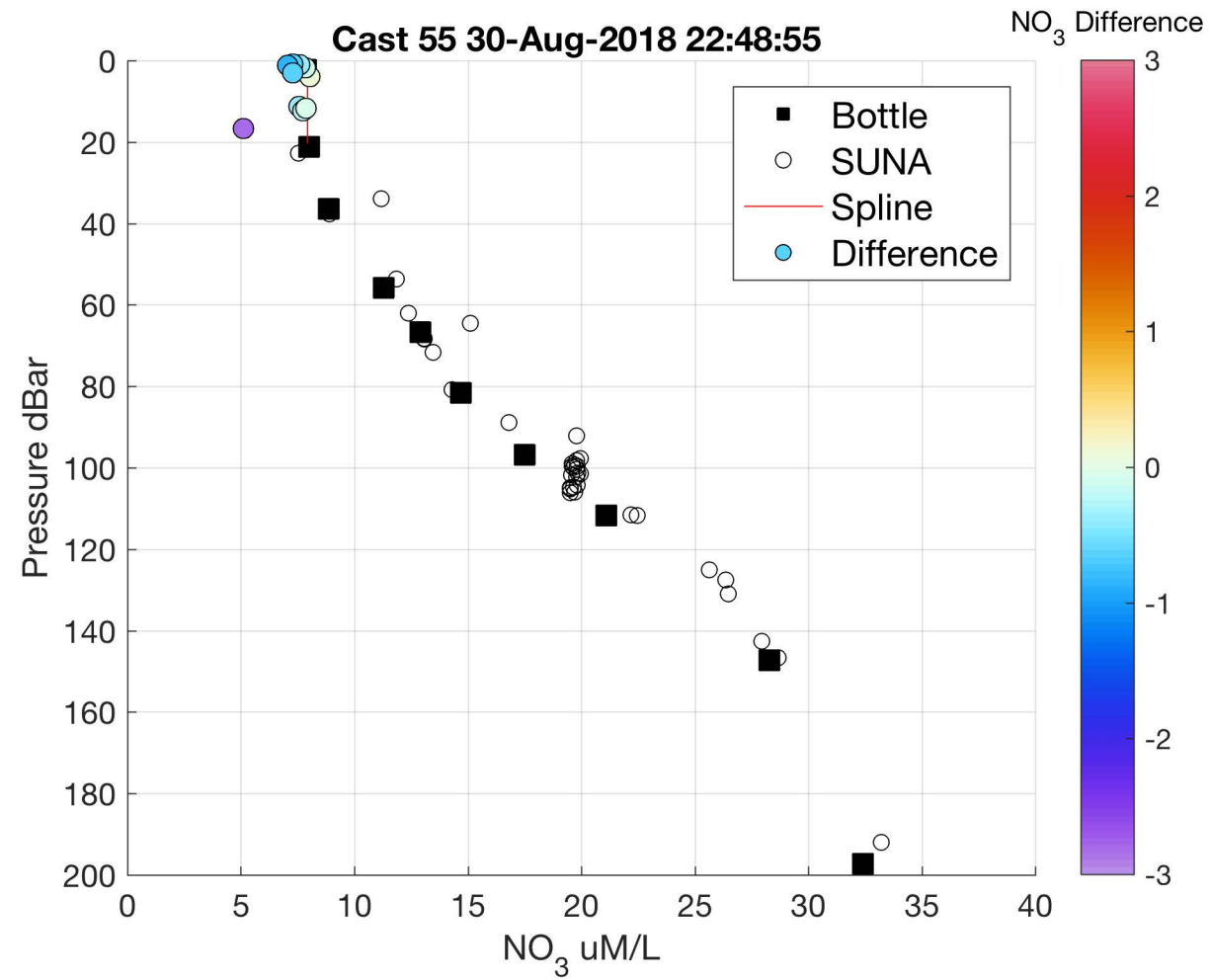


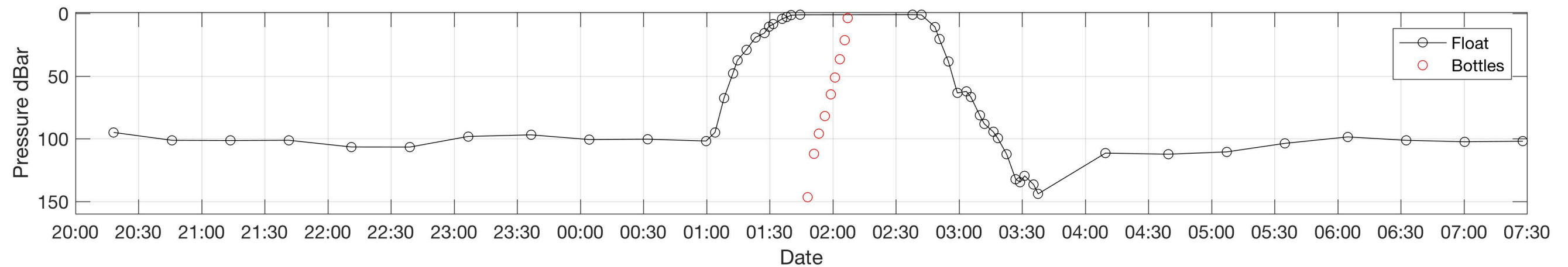
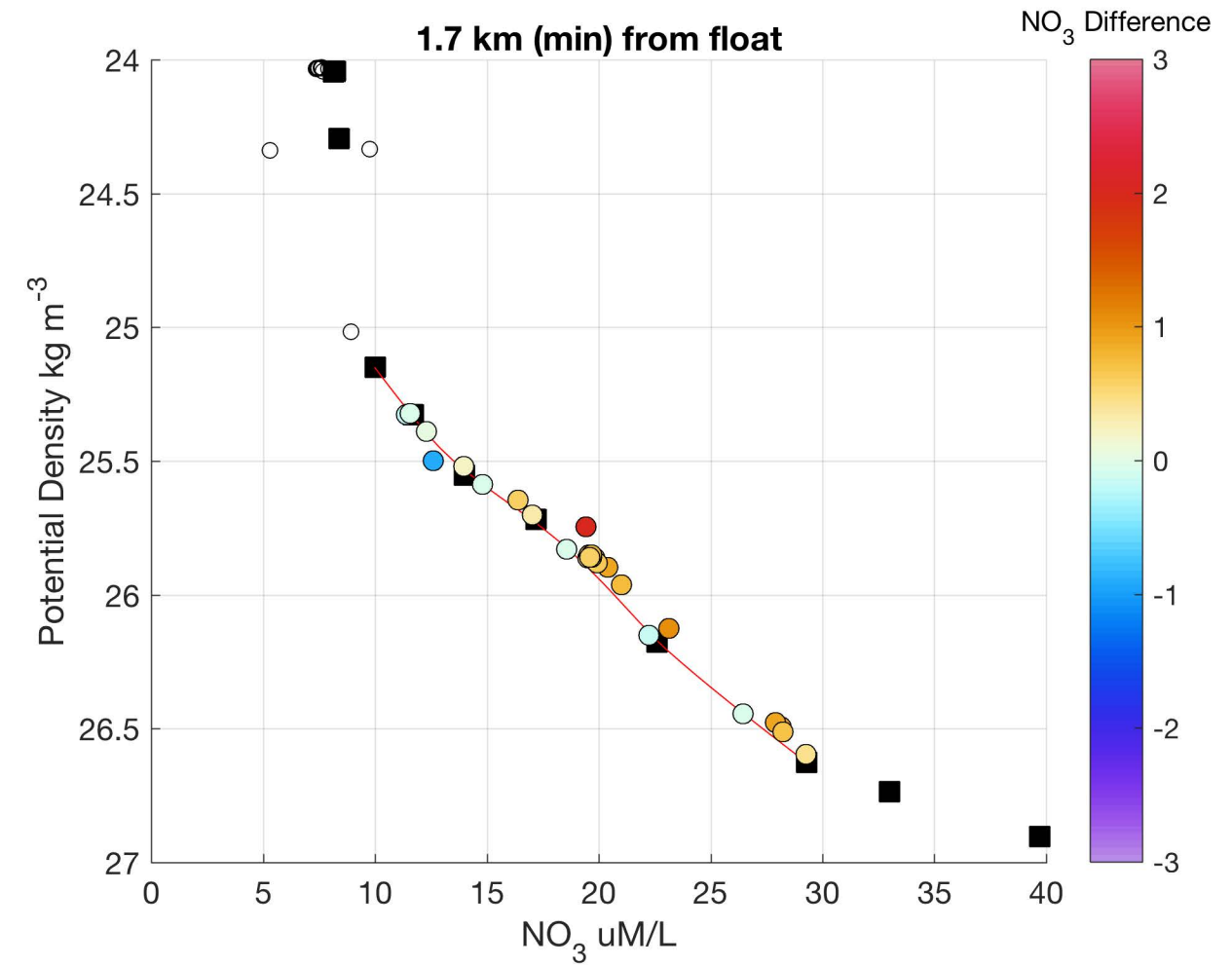
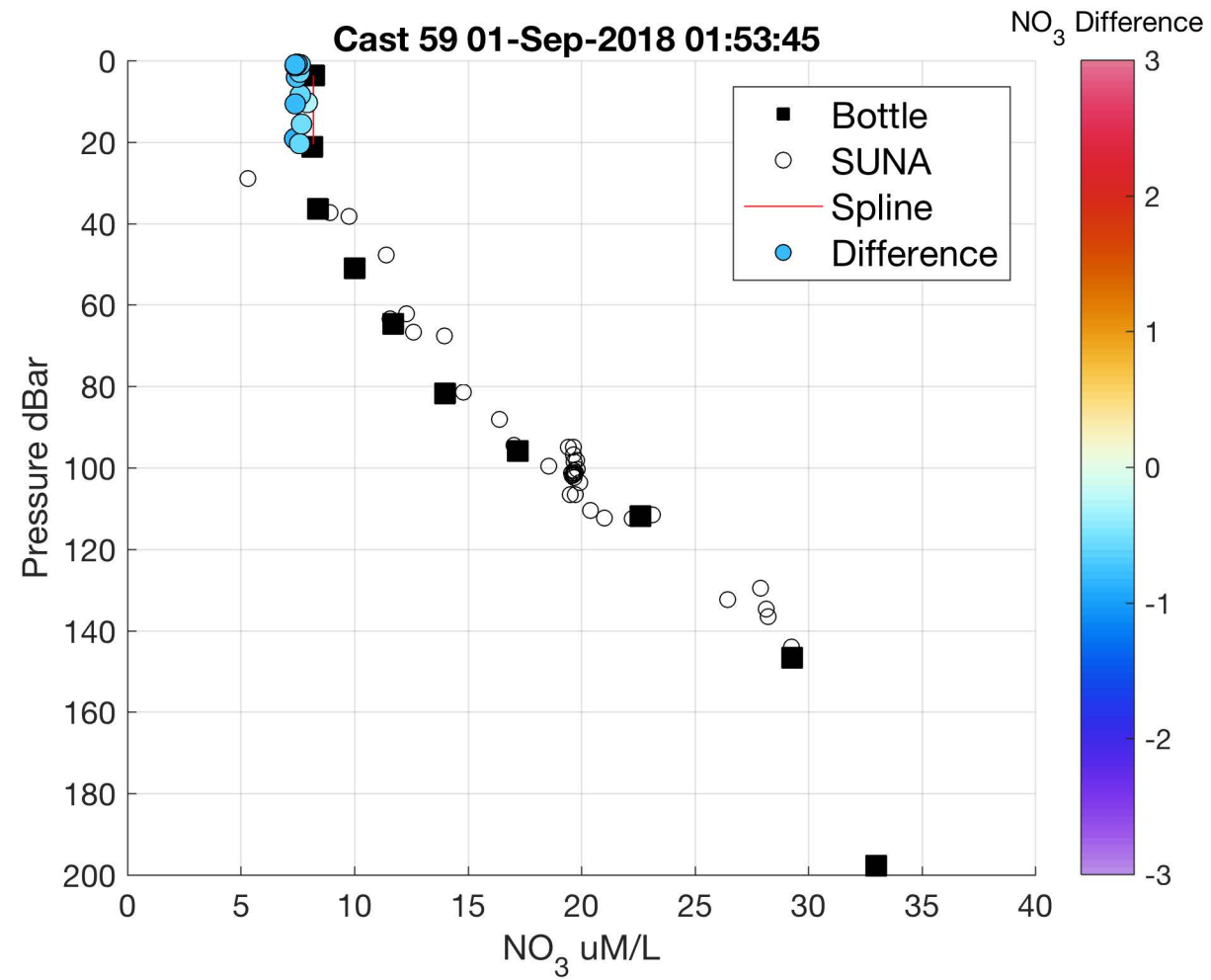


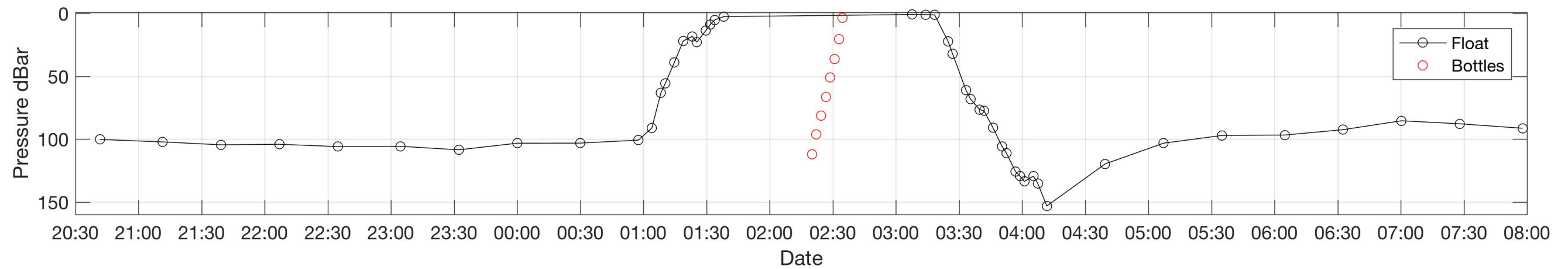
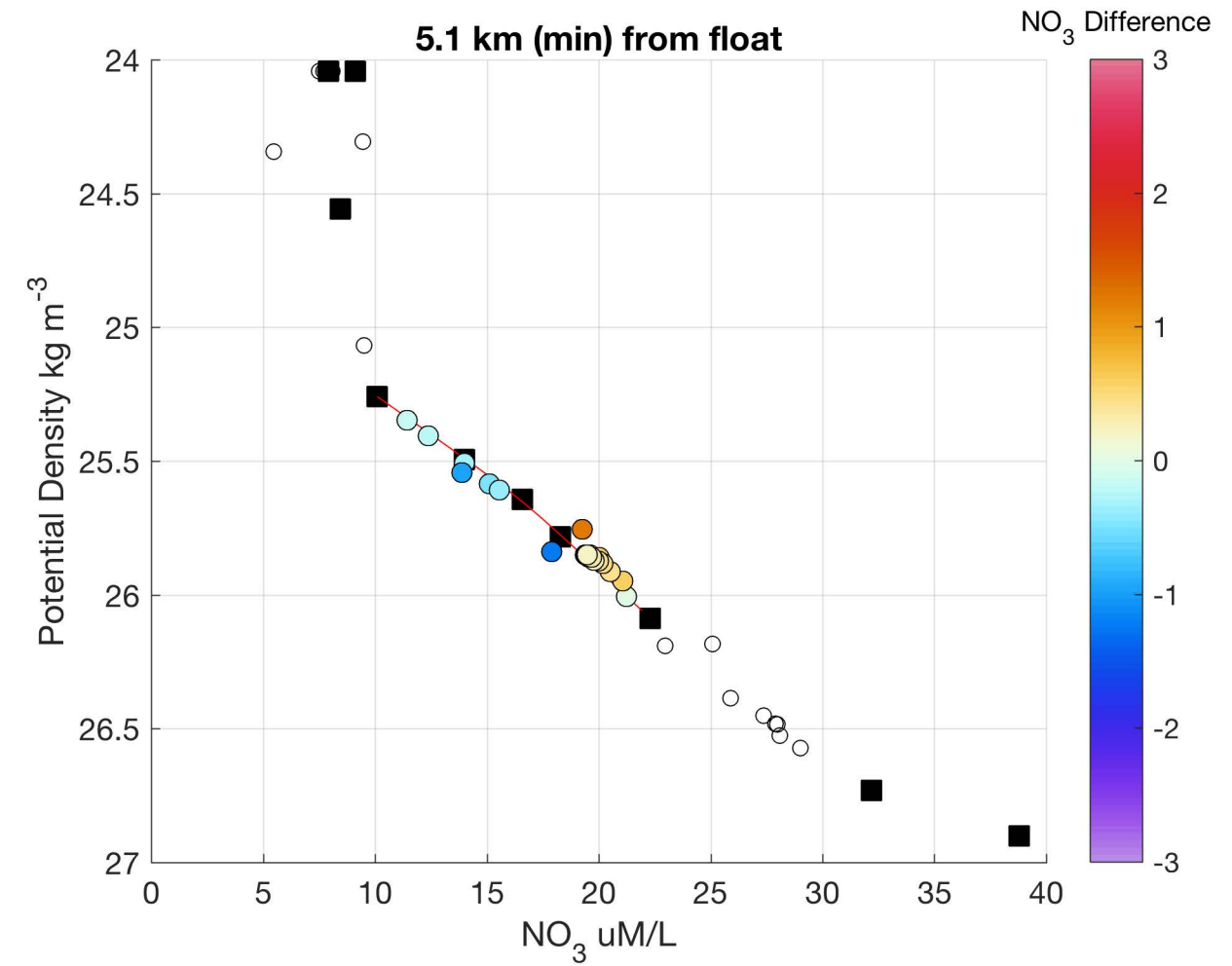
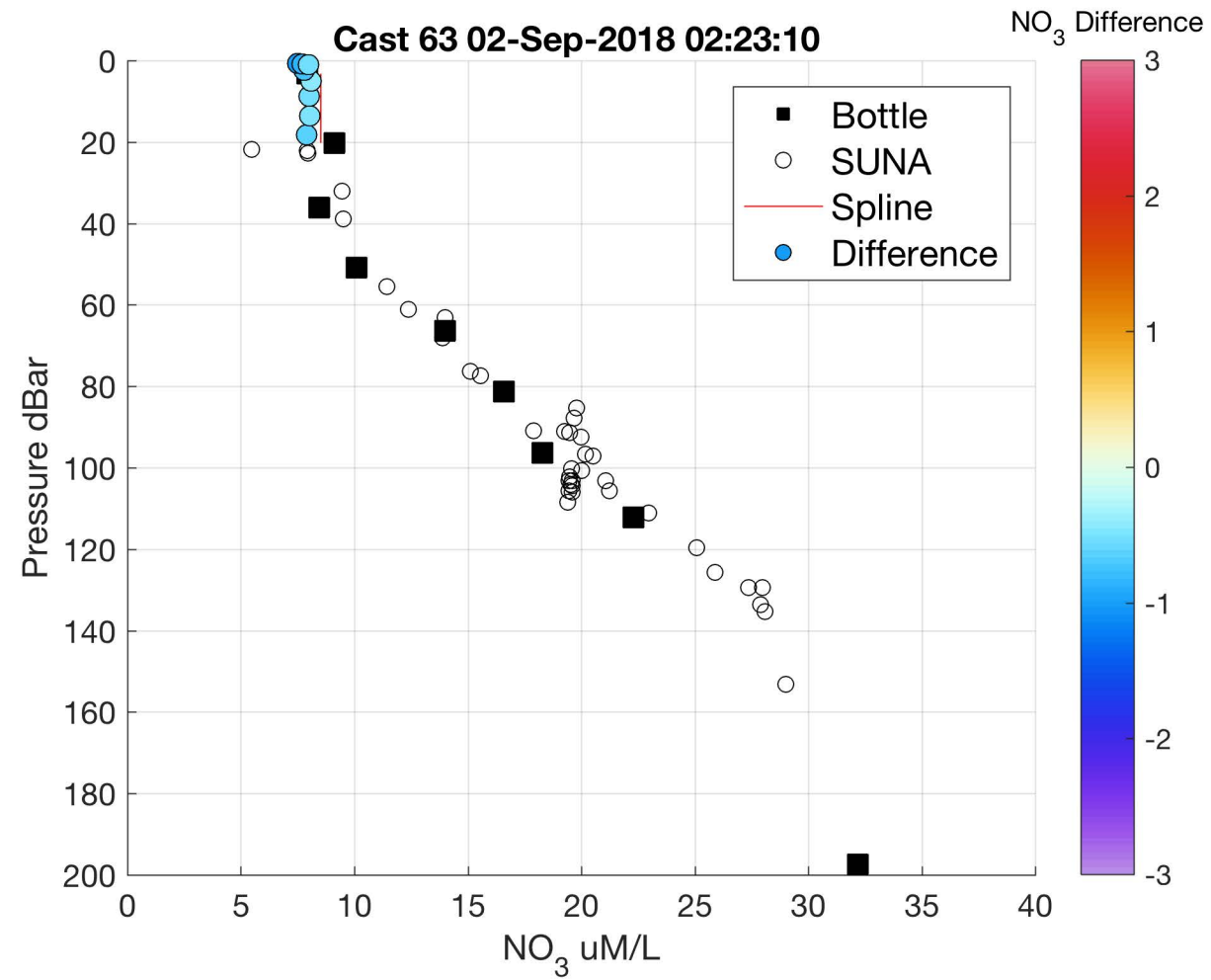


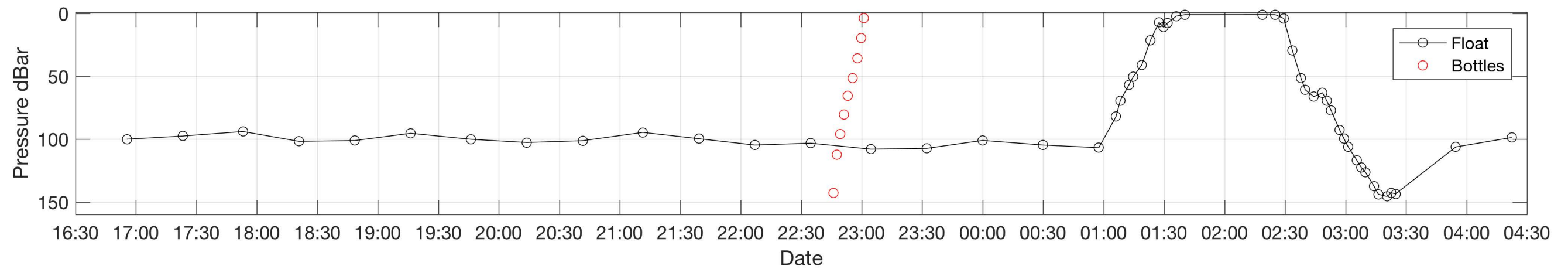
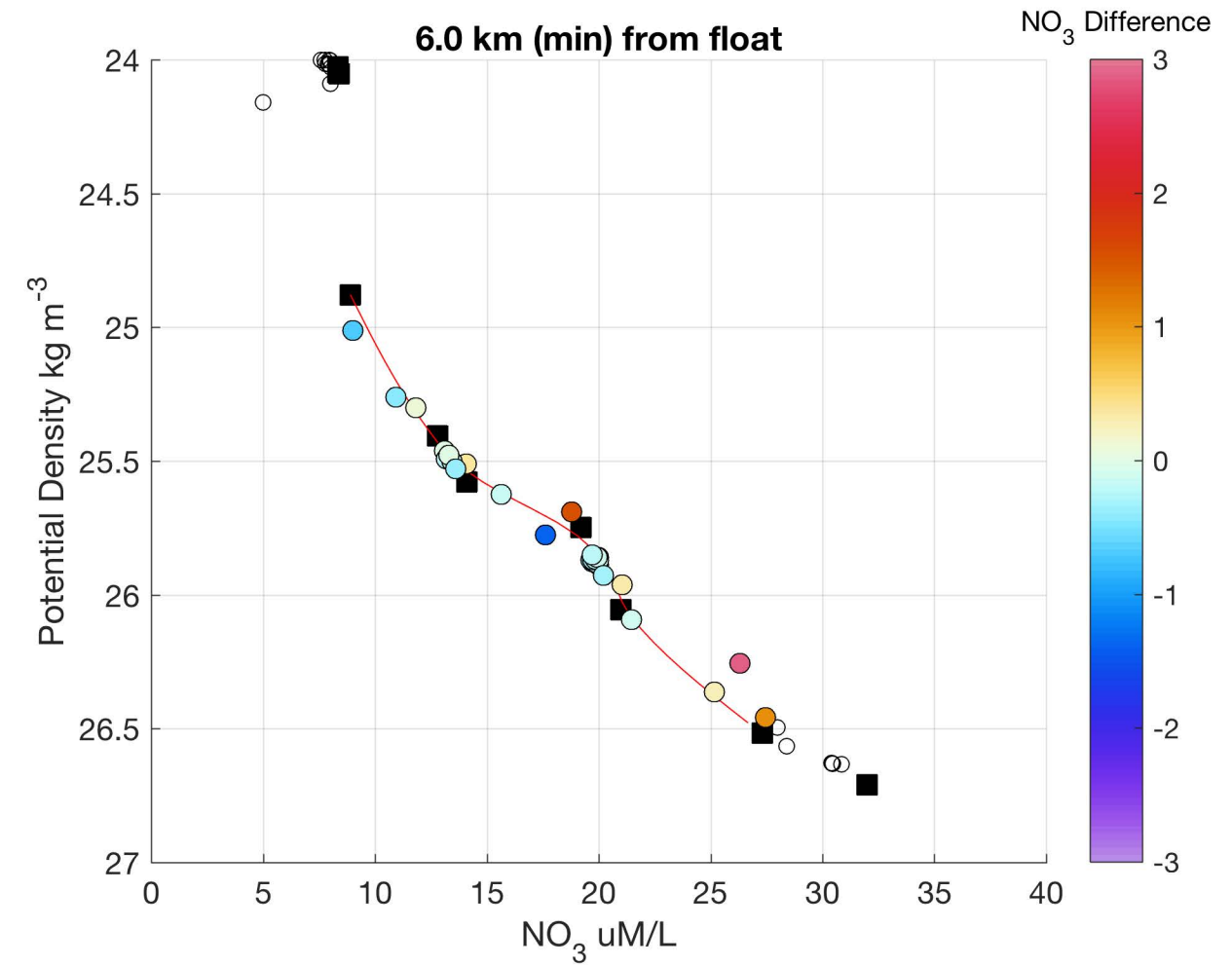
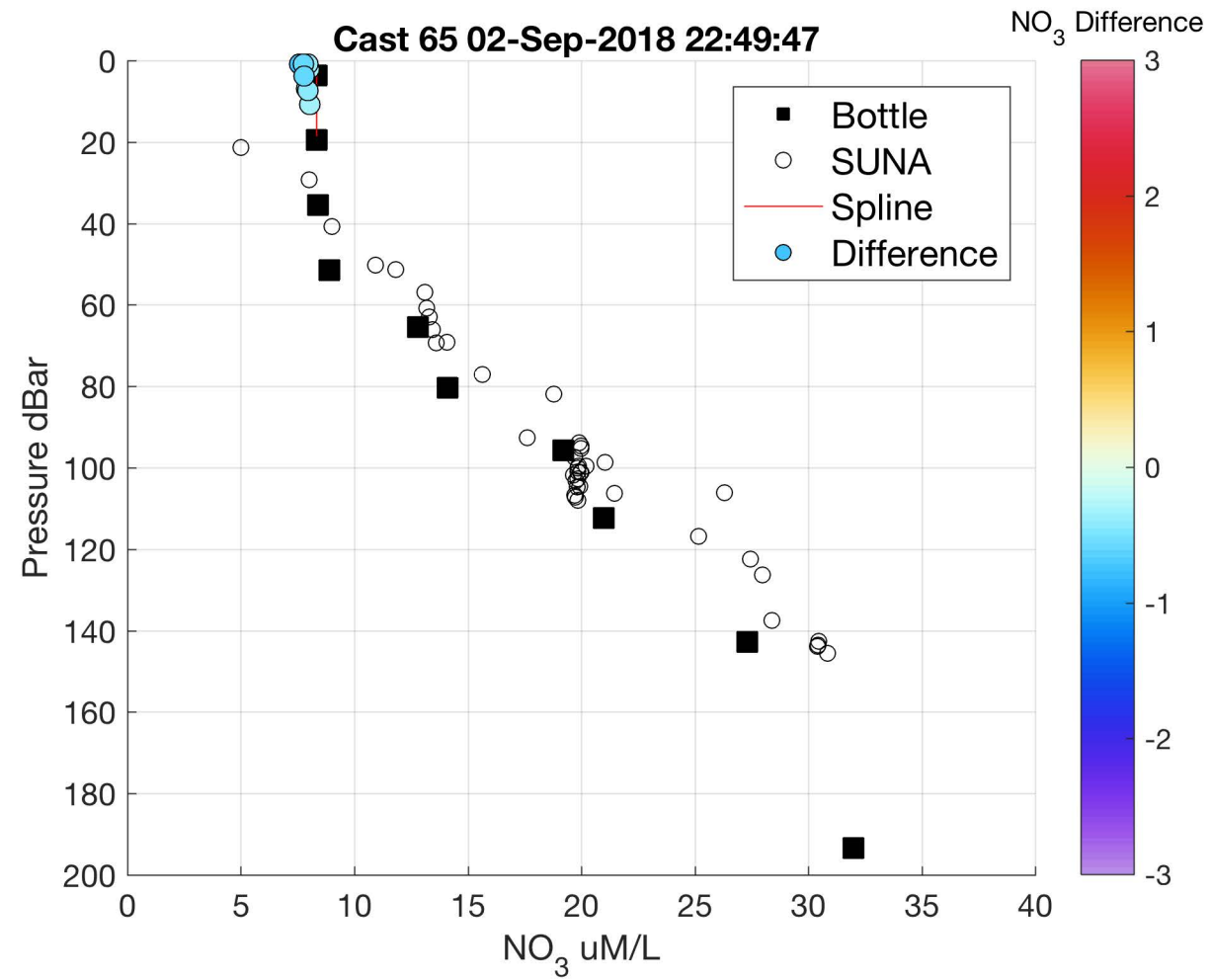




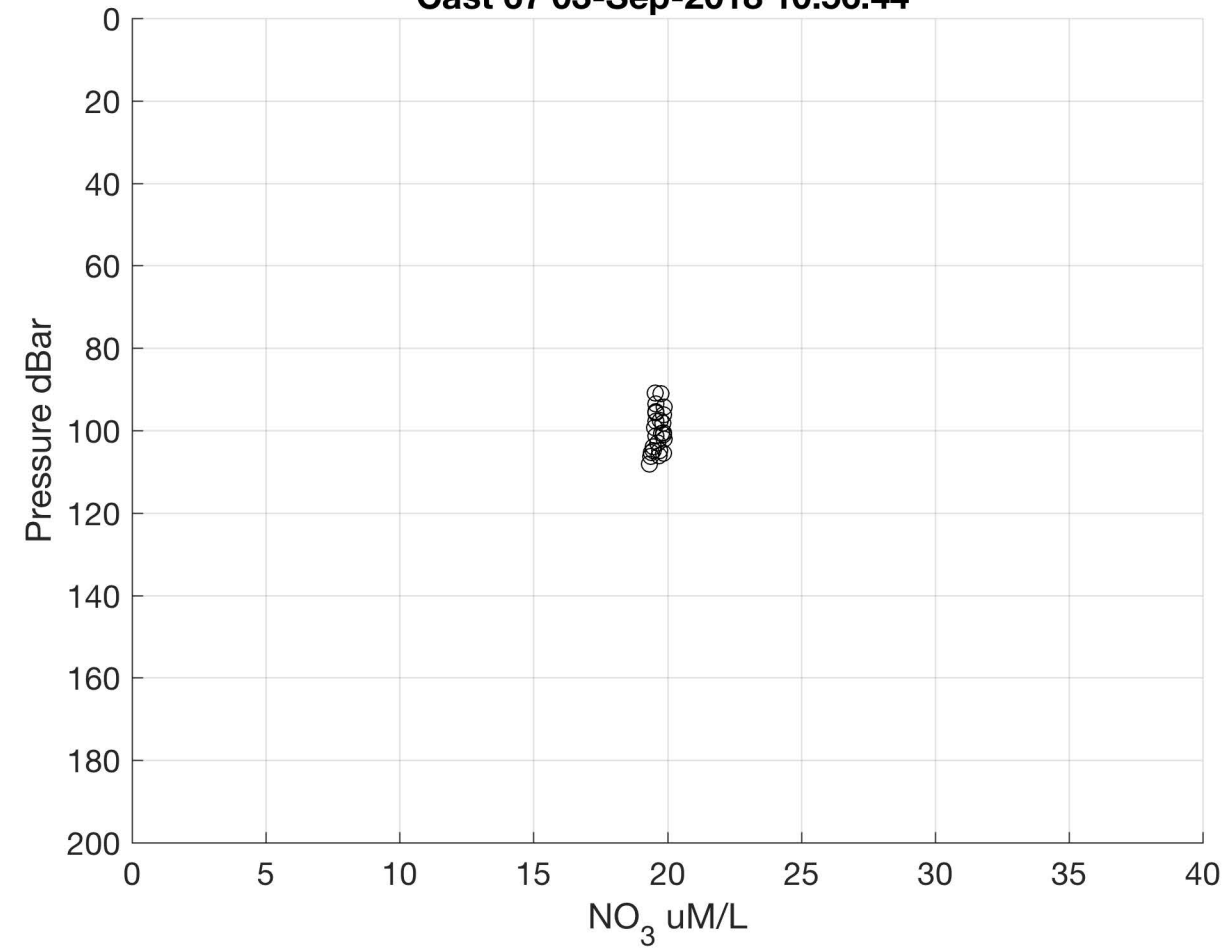








Cast 67 03-Sep-2018 10:56:44



5.4 km (min) from float

